



## **Arsenic removal from water using seawater-neutralised red mud (Bauxsol)**

**Genc Fuhrman, Hülya**

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**Environment & Resources**  
Technical University of Denmark

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Hülya Genç Fuhrman



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**Hülya Genç Fuhrman**

**PhD thesis, January 2004**

**Environment & Resources DTU  
Technical University of Denmark**

***Arsenic removal from water using seawater-neutralised  
red mud (Bauxsol)***

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## Preface

This thesis is based on the research done for a PhD project undertaken from January 2001 to January 2004 at Environment & Resources DTU, Technical University of Denmark. The supervisors are Professor Jens C. Tjell from Environment & Resources DTU, Professor David McConchie from Southern Cross University in Australia, and Professor Olaf Schuiling from IHE Delft, in The Netherlands. The project was funded by Virotec Int., Australia and a travel grant for participating to a conference was given by Otto Mønstedts Fond, Denmark. Furthermore, Geochem/SELOR, The Netherlands is also acknowledged for partial financial support.

The thesis is composed of a summary of the subject “Arsenic removal from water using seawater-neutralised red mud (Bauxsol)” as well as four journal papers (three published, and one submitted for publication in international peer-reviewed journals), and two conference papers also peer-reviewed and published in special journal issues. The papers are not included this www-version, but they can be obtained from the Library at Environment & Resources DTU, Bygningstorvet, Building 115, Technical University of Denmark, DK-2800 Lyngby ([library@er.dtu.dk](mailto:library@er.dtu.dk)). The in-text references and the titles of the papers are:

(**I**: Genç et al., 2003; **II**: Genç and Tjell, 2003; **III**: Genç-Fuhrman et al., 2004; **IV**: Genç-Fuhrman et al., 2004a; **V**: Genç-Fuhrman et al., 2004b; and **VI**: Genç-Fuhrman et al., 2004c).

- I.** Genç, H.; Tjell, J.C.; McConchie D.; Schuiling, O.; 2003. Adsorption of arsenate from water using neutralised red mud. *Journal of Colloid and Interface Science*, **264**, 327-334.
- II.** Genç, H.; Tjell, J.C.; 2003. Effect of phosphate, silicate, sulfate, and bicarbonate on arsenate removal using activated seawater neutralised red mud (Bauxsol). *Journal of Physics IV*, **107**, 537-540.
- III.** Genç-Fuhrman; H., Tjell, J.C.; McConchie, D.; 2004. Increasing the arsenate adsorption capacity of neutralised red mud (Bauxsol). *Journal of Colloid and Interface Science*, **271**, 313-320.
- IV.** Genç-Fuhrman, H.; Tjell, J.C.; McConchie, D.; 2004a. Adsorption of arsenic from water using activated neutralised red mud. *Environmental Science and Technology*, **38**, 2428-2434.
- V.** Genç-Fuhrman, H.; Tjell, J.C.; McConchie, D.; 2004b. Arsenic removal from drinking water using activated red mud. *Malaysian Journal of Science*, **23**, 219-228.
- VI.** Genç-Fuhrman, H.; Bregnhøj, H.; McConchie, D.; 2004c. Arsenic removal from water using sand-red mud columns. *Water Research*, submitted.

During this PhD study I have carried out an extensive laboratory study, participated in two international conferences, where I gave oral presentations, and visited two universities, University of Oxford Department of Earth Sciences (in England) for four months and Southern Cross University Environmental Research Group (in Australia) for two months. I have also been a member of a research group “Sustainability and Development” at Environment & Resources DTU, and contributed to international journals.

I would like to thank my supervisors Jens C. Tjell, David McConchie and Olaf Schuiling for their support throughout the study. I would also like to thank all my colleagues at Environment & Resources DTU, especially to Hans Mosbæk, Henrik Bregnhøj, Susanne Kruse, Henriette Blankenstejner, Anitha K. Sharma and Camilla Hedberg.

The hospitality I received from Greg Maddocks, Malcolm Clark, Tom Ryfell, Graham Lancaster and Sarah Pope at Southern Cross University, and from Don Fraser at Oxford University during my visits to these universities is also greatly acknowledged.

My thanks are also to my friends all around the world.

Very special thanks to my husband David for his love and support throughout and to my family back in Turkey.

*Sevgili anneme, babama ve kardeşlerime beni her zaman destekledikleri ve hep karşılıksız yürekten verdikleri için çok teşekkür ederim...*

Kgs. Lyngby January 30, 2004

Hülya Genç Fuhrman

*to David*

## Abstract

This thesis presents the results of a detailed study on “arsenic removal from water using seawater-neutralised red mud (Bauxsol™)”, and incorporates six papers that describe and discuss the experimental work carried out as part of the PhD project.

Increasingly stringent legislation on the permissible concentrations of arsenic in drinking water has led to increased investigations of the occurrence, chemical speciation and mobility of arsenic in natural waters and of methods for removing arsenic during water treatment. Epidemiological studies suggest that there are significant health risks, including cancer, associated with prolonged exposure to elevated arsenic concentrations in drinking water even at quite low concentrations. Although background arsenic concentrations in natural environments are usually low, arsenic concentrations are high in many parts of the world due to mobilisation from natural geological sources or at a smaller scale from industrial pollution. While arsenic associated with industrial pollution can be managed by improving process engineering and environmental management practices, making water that has a naturally high arsenic content safe to drink requires some form of water treatment to reduce arsenic concentrations. This study addresses the water treatment approach and focuses on developing new arsenic removal technologies that use the red mud residues from bauxite refineries as a new sorbent.

Arsenic can exist in natural waters in both organic and inorganic forms, however only the inorganic forms, arsenate (As(V)) and arsenite (As(III)), are considered in this study because all available data indicate that the amount of organic arsenic in drinking water sources is insignificant. The experiments carried out during this study address the removal of both arsenate and arsenite using Bauxsol and new sorbents developed during the study as derivatives of Bauxsol. The study examines both arsenate and arsenite, but the greatest emphasis is placed on the arsenate because both the published literature and the preliminary part of this study indicate that it is very difficult to adsorb uncharged arsenite at near neutral pH values and that the simplest approach is to oxidise arsenite to arsenate for efficient sorption.

In this study seawater-neutralised red mud (Bauxsol) is used under a wide range of experimental conditions and it is found that Bauxsol removes arsenate much more effectively than unneutralised red mud. Neutralisation of the caustic red mud is an essential step in developing an effective arsenic adsorbent from red mud. Seawater-neutralisation increases the calcium content of red mud and data obtained during this study show that the presence of calcium has a positive effect on the arsenic removal. Seawater-neutralisation also decreases the pH of red mud from about 13 to 8.2 - 8.8. The removal of arsenate from water using Bauxsol is sensitive to several parameters tested, including pH, ionic strength, adsorbent dosage, initial arsenate concentration and the source water composition. Arsenate is an anion in a wide pH range, and its increasing adsorption with decreasing pH indicates ligand-like adsorption. The adsorption is independent of ionic strength, suggesting the formation of inner-sphere complexes. Lower arsenate concentrations and higher adsorbent dosages enhanced arsenate removal, but high adsorbent dose rates are not practical. Because the experiments are carried out using deionised water, the effect of other ions likely to be

present in potable water is also investigated. Tests conducted with added  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ , or  $\text{Cl}^-$  showed that under the experimental conditions used,  $\text{Ca}^{2+}$  increases arsenate removal possibly due to the increase in the positive charges on the Bauxsol surface, while  $\text{HCO}_3^-$  reduces arsenate removal, and  $\text{Cl}^-$  has a negligible effect on arsenate removal. This part of the study concluded that Bauxsol had a good arsenate removal capacity when sufficient adsorbent was used i.e.  $> 5 \text{ g/L}$ , but it is not yet able to compete with other widely used adsorbents. Thus, either Bauxsol could be used as a cost-effective pre-treatment method before applying other more costly arsenate removal methods, or its sorptive capacity could be increased to make it competitive with other conventional sorbents.

The possibility of increasing the arsenate sorption capacity of Bauxsol is investigated in the second part of this study, where acid treatment, combined acid and heat treatment and addition of ferric or aluminum sulfate are tested. When acid treatment or combined acid and heat treatment are applied, the arsenate removal capacity of Bauxsol is significantly increased together with the reactive surface area of the sorbent. Of these acid and heat treated Bauxsol, herein named activated Bauxsol (AB), was the most effective possibly because the heat treatment allowed the Bauxsol to develop more porosity. Unexpectedly, the addition of ferric or aluminum sulfate reduced the arsenate removal capacity of the sorbent. Several reasons are proposed for the reduction of arsenate removal when ferric or aluminum sulfate are added, but it is most likely caused by the formation of a gelatinous precipitate that occludes some of the potential sorptive sites; the use of ferric chloride may provide an alternative worthy of future investigation. In this study the results clearly indicate that, of the sorbents tested, AB has the highest affinity for arsenate and that AB can perform very effectively even in the presence of competing anions including, phosphate, silicate, sulfate, and bicarbonate. With the promising results obtained for using AB in this part of the study, further investigations were designed to elucidate the sorptive characteristics of the AB adsorbent to understand how it worked and to optimise its performance.

In the third stage of this study, detailed laboratory investigations were carried out to develop an understanding of arsenic removal using AB; in this work the removal of arsenite by AB is studied in addition to the removal of arsenate. Arsenic removal is tested under different pH, adsorbent dosage, initial arsenic concentration, temperature, ionic strength and particle size conditions. As with ordinary Bauxsol, arsenate removal using AB is favoured by decreasing pH, and ionic strength had minor effect, suggesting ligand-like adsorption and inner-sphere complex formation, respectively. Higher temperatures favoured arsenate removal, whereas initial arsenate concentration had no effect on the removal efficiency, and the adsorbent particle size had only a minor effect. When the adsorbent dosage is increased, arsenate removal also increased, but it was found that if arsenic exists in the arsenate form, adsorbent dosages as low as  $0.4 \text{ g/L}$  are enough to achieve WHO standards  $0.01 \text{ mg/L}$  under pH and initial arsenate concentration conditions similar to real life conditions. Arsenite adsorption on the other hand, is favoured by slightly alkaline pH values with maximum adsorption recorded at pH 8.5; arsenite removal decreased with increasing initial arsenite concentration. Overall, AB was found to be a very effective adsorbent especially for arsenate removal from water with a sorptive capacity comparable to other conventional sorbents.

The effect of the source water composition on the effectiveness of an absorbent is also important and thus the fourth phase of the study investigates the possible influence of anions in the water on arsenic removal efficiency. The study investigated the influence of phosphate, silicate, sulfate and bicarbonate when present separately and in combination; the tests were conducted at several arsenate and anion concentrations and solution pH values. The results obtained were in agreement with data published elsewhere and indicate the important effect of source water composition on arsenic removal. All tested anions suppressed the arsenic removal with a decreasing order on molar basis of phosphate > silicate > sulfate > bicarbonate. Moreover, when initial arsenate concentration is increased the anion suppression is also increased, and when the combined effects of the anions are tested it is found that despite the insignificant effect of bicarbonate and sulfate when added alone, they have a larger suppression effect when they coexist with phosphate and silicate.

Because both Bauxsol and AB are produced from an industrial residue, these sorbents could introduce unwanted contaminants to the water. A wide range of elements was investigated, and it is found that neither Bauxsol nor AB caused any secondary pollution of the water as a consequence of the treatment to remove arsenic. Moreover, desorption studies indicated that the bound arsenate can not be easily leached out; a maximum desorption of only 40% could be achieved and that required raising the pH to 11.6 (much less arsenate could be desorbed under lower pH conditions). Despite their high arsenic removal efficiency, neither AB nor Bauxsol would be practical sorbents if they became toxic after use because the disposal of the toxic waste would introduce additional costs and environmental problems. Therefore, the toxicity characteristic leaching procedure (TCLP) test was applied to the spent sorbents, and the results indicated that neither of them was toxic; indeed the amount of arsenic that could be released during the TCLP leach test was exceptionally low. This finding is considered to be particularly important in view of the possible application of the sorbent.

In the final part of the study, column experiments were conducted to test the sorbents under continuous flow conditions and for this part of the study two new sorbents were developed from Bauxsol and AB. The new products, Bauxsol coated sand (BCS) and AB coated sand (ABCS), were developed because the fine texture of Bauxsol and AB makes them difficult to use in column studies. The results of this work show that higher sorptive capacities are evident in column experiments compared to the batch tests. Thus, using BCS or ABCS for water treatment purposes under continuous flow conditions is particularly promising for practical water treatment applications. Higher bed volumes can be achieved before breakthrough. It is partly possible to desorb arsenate from the BCS and ABCS, which is a prerequisite for regeneration, but detailed BCS and ABCS regeneration studies have not yet been carried out.

Among the various technologies available for arsenic removal, adsorption has recently emerged as the most favoured option, as it is easily applicable in small scale and offers endless possibilities of developing cost-effective new adsorbents. In this context, this study has shown that Bauxsol, AB, BCS and ABCS are highly effective new adsorbents especially for As(V) removal. However, full scale field trials using Bauxsol, AB, BCS and ABCS are still required to evaluate their suitability for use under practical conditions.

## Dansk Résumé

Denne afhandling viser resultaterne af studiet "Arsenfjernelse fra vand ved hjælp af havvands-neutraliseret "rødt mudder" (Bauxsol)". Rødt mudder er den stærkt basiske remanens efter basisk kogning af Bauxit mineraler for opløsning af aluminiumoxider. Afhandlingen inkluderer 6 artikler som beskriver og diskuterer det eksperimentelle arbejde i dette ph.d. projekt.

Baggrunden for arbejdet er de stadigt strengere krav til det tilladelige indhold af det giftige arsen i drikkevand. En naturlig følge er en stigende interesse til forekomst, kemisk speciering og mobilitet af arsen i naturlige vande, samt udvikling af metoder til fjernelse af stoffet fra vand. Epidemiologisk medfører indtagelse af arsen svære helbredsskader på mennesker selv ved relativt lave koncentrationer i drikkevand i længere tid. Herunder findes mange kræfttilfælde i indre organer hos eksponerede personer.

Naturlige vandforekomster, specielt overfladevand, er oftest fri for generende arsen koncentrationer. I mindre områder kan findes industriel forurening med høje koncentrationer. De største problemer med arsen i vand og drikkevand findes i grundvand i floddeltaer, hvor brønde og borer er konstrueret til udvinding af mikrobiologisk sikkert drikkevand. Her er mobilisering af arsen i sedimenterne til grundvandet en trussel mod folkesundheden for 30-50 millioner mennesker globalt, med de fleste tilfælde i Bangladesh og Vestbengalen i Indien.

Arsen kan forekomme i både uorganiske former og som organiske forbindelser i vand. I dette arbejde behandles kun de uorganiske former arsenat ( $\text{As(V)}$ ) og arsenit ( $\text{As(III)}$ ), da kun disse menes at kunne påvirke menneskets helbred i de forekommende koncentrationer. I arbejdet er undersøgt fjernelsen af begge former fra vand ved hjælp af Bauxsol og nyudviklede sorbenter baseret på Bauxsol. Der er lagt mest vægt på fjernelsen af arsenat da det ifølge litteraturen og de preliminaire undersøgelser klart har vist at den uladete specie arsenit ikke er let at fjerne ved nær-neutrale pH værdier uden forudgående oxidation til arsenat.

Rødt mudder er her undersøgt for dets evne til at binde arsenat under vidt forskellige omstændigheder. Det ubehandlede materiale (rødt mudder) binder arsenat langt svagere end efter havvandsneutralisering (Bauxsol). Ved neutraliseringen sænkes pH fra ca. 13 til 8.2 - 8.8 og samtidig fældes og bindes en del calcium i materialet som forøger materialets evne til at binde arsenat betydeligt. Materialets evne til at binde arsenat er desuden afhængig af pH, dosering, start koncentration af arsenat og koncentration af andre ioner i vandet. Den stærkere binding ved lavere pH og næsten uafhængighed af ionstyrke indikerer en ligand-agtig binding og inner-sfære komplekdannelse. Lave arsenat koncentrationer og høje doseringer af sorbent forøger arsenatfjernelsen fra vand. Andre normale ioners tilstedeværelse ændrer arsenat adsorptionen; således forøger  $\text{Ca}^{2+}$  absorptionen, mens  $\text{HCO}_3^-$  nedsætter absorptionen, og  $\text{Cl}^-$  er uden indvirkning. Denne første del af studiet viser at Bauxsol kan fjerne Arsenat ved relativt høje doseringer ( $> 5 \text{ g/L}$ ) dog uden at være bedre end andre kendte sorbenter.



I den anden del af studiet er undersøgt mulighederne for at øge arsenatbindingen ved behandling af Bauxsol'en med syre, syre + ophedning, eller behandling med Al- og Fe-salte. Den absolut største forbedring i arsenatbindingen fandtes i den kombinerede behandling med syre og ophedning, hvor det specifikke overfladeareal samtidig forøgedes betydeligt. Dette bedste produkt kaldes aktiveret Bauxsol (AB). Al- og Fe-salte formindskede uventet arsenatbindingen betydeligt. Årsagen hertil er uklar, men sandsynligvis er dannelse af hydroxid-geler i porer i Bauxolen blokerende for adsorptionen. AB er klart den bedste af de undersøgte sorbenter, med en evne til at binde arsenat også ved tilstedeværelsen af konkurrerende ioner som fosfat, silikat, sulfat og bikarbonat.

De videre undersøgelser blev derfor koncentreret om en nøjere undersøgelse af arsenbindingens karakter på AB for en klarere forståelse af de involverede mekanismer, og som forudsætning for en optimering af en praktiske udnyttelse. I denne tredje del blev både arsenat og arsenits binding til AB studeret på samme måde som tidligere for almindelig Bauxsol. Arsenat bindes stærkere ved lavere pH, mens ionstyrken havde lille effekt. Forhøjet temperatur forøger kapaciteten, mens begyndelseskonzentration og partikkelstørrelse har lille effekt. Arsenat kan fjernes effektivt ned til den nuværende grænseværdi for As på 10 µg/L med anvendelse af 0.4 g/l AB fra 330 µg/L. Arsenit fjernes bedst ved lidt højere pH med maximum omkring pH = 8.5, men den absolutte kapacitet for fjernelse af arsenit er lav sammenlignet med kapaciteten for arsenat.

Som den fjerde indsats i arbejdet blev gennemført en nøjere undersøgelse af de normalt i råvand forekommende anioners interferens på arsenat adsorptionen på AB. Rangordenen for nedsættelse af ABs kapacitet er fosfat > silikat > sulfat > bikarbonat på molær basis. Ved højere arsenat koncentrationer er interferensen mere udtalt. Effekten af de to svagest interfererende sulfat og bikarbonat stiger væsentligt hvis de optræder sammen med de stærkest interfererende.

Da råmaterialet for de her udviklede og undersøgte sorbenter er et affaldsprodukt blev det endvidere undersøgt om brugen til behandling af vand kan medføre forurening med uønskede og giftige stoffer. For en lang række undersøgte stoffer kunne der ikke konstateres afsmittning hvilket peger på at Bauxsol og AB begge er stærkt bindende sorbenter for mange stoffer. Også arsenat er svært at fjerne fra en brugt sorbent. Selv ved en kras behandling ved pH = 11.6 kan kun 40% fjernes. En mulig udvaskning efter placering i en losseplads er også undersøgt ved TCLP proceduren (toxicity characteristic leaching procedure). Der fandtes ikke stoffer der overskred grænseværdierne ved denne test. Der er dermed ikke konstateret ubehagelige sideeffekter hverken af den primære anvendelse af disse sorbenter til rensning af drikkevand eller ved bortskaffelsen brugt sorbent.

## 1. Introduction

Arsenic (As) contamination of drinking water is a major health concern, because drinking arsenic contaminated water is linked to several types of cancers. Unfortunately, there is no known cure for arsenic poisoning and therefore providing arsenic free drinking water is the only way to diminish the adverse health affects of arsenic. Consequently, several methods are proposed to provide arsenic-free water. These methods suggest either the treatment of arsenic contaminated groundwater, or looking for the alternative options (e.g. surface water treatment, rain-water harvesting, etc). The use of alternative water sources, however, can only be possible after a major and costly technological shift and thus, the treatment of arsenic contaminated water to the guideline values is the preferred option (Ahmed, 2003). High concentrations of arsenic in water and soil have been documented in Taiwan, Argentina, the USA, Chile and many other countries (Table 1), but of these, the most severe outbreaks of arsenic poisoning have been associated with groundwaters in the Bengal Delta including Bangladesh and West Bengal (Eastern India) where an estimated total of 120 million people (80 million in Bangladesh, 40 million in India) are at risk (Chowdhury et al., 2000). Arsenic contamination in the affected districts of the Bengal Delta is potentially the greatest environmental calamity ever reported (Karim, 2000).

Arsenic is an environmental health concern, because long-term epidemiological studies demonstrate that it is toxic to humans and other living organisms. Arsenic is also a social concern in Bangladesh because women affected by arsenic are reportedly discriminated against in their working environments and many have to leave their jobs when skin changes caused by arsenic contaminated water become apparent, leading to economic hardship and social disruption (The Daily Star, 2003).

Background arsenic concentrations in natural water are low (Clesceri, et al., 1992), but elevated arsenic concentrations are common in groundwater as a result of natural conditions or anthropogenic impacts. Natural oxidation and/or reduction reactions involving arsenic-bearing rocks under favourable Eh and pH conditions may mobilize the arsenic and increase arsenic concentrations in groundwater. Human activities that could increase arsenic concentrations in groundwaters and surface waters include; oil and coal burning power plants, waste incineration, cement works, disinfectants, household waste disposal, glassware production, electronics industries, ore production and processing, metal treatment, galvanizing, ammunition factories, dyes and colours, wood preservatives, pesticides, pyrotechnics, drying agents for cotton, oil and solvent recycling and pharmaceutical works (Bothe and Brown, 1999; Matschullat, 2000; Berg et al., 2001). For more information on the natural and anthropogenic sources of arsenic see the excellent reviews of Matschullat (2000), and Bissen and Frimmel (2003).

When water is contaminated with arsenic it cannot be seen, because arsenic is invisible and does not affect the taste or smell of the water unless concentrations are extremely high. Exposure to arsenic by the general population can take place in several different ways, but consuming arsenic-containing water and food (especially marine food) are the most common routes. The extent of exposure can be estimated by determination of the arsenic concentration in hair, nails (arsenic accumulates in hair and nails because of the high content of keratin) and urine (to assess the recent exposure) (Ritsema and Heerde,

1997; Le, 2002). Although beneficial effects have been reported for some arsenic compounds e.g. reduction of fever, prevention of black-death, healing of boils, and treatment of chronic myelocytic leukaemia (Goessler and Kuehnelt, 2002), the adverse health effects of arsenic are much more common. While acute arsenic poisoning can lead to rapid death, chronic negative health impacts are more common and tend to appear only after several years of exposure (Hanchett et al., 2002). The most commonly observed symptoms identifying people suffering from chronic arsenic poisoning are arsenical skin lesions (e.g. melanosis, keratosis), blackfoot disease, and in more serious cases, incidents of gangrene, skin cancer (when ingested), and lung cancers (when inhaled) (Das et al., 1995; Karim, 2000; Hanchett et al., 2002). It is noted, however, that no clear correlation between arsenic concentrations in water and skin cancer has been reported in the USA (see Valberg et al., 1998) suggesting that other factors may affect the link between arsenic intake and skin cancer; e.g. dietary factors (Das et al., 1995).

It is important to note that the most effective way to overcome the adverse health effects of arsenic is prevention of further exposure by providing safe drinking water, because there is no effective treatment to counteract arsenic toxicity. Therefore, the World Health Organization (WHO, 1993) has recommended a maximum contaminant level (MCL) for drinking waters of 0.01 mg/L. Many countries however, permit higher arsenic concentrations in drinking water mainly due to the high cost of treatment to lower concentrations. As noted by Gregor (2001) the MCL value is the concentration below which the presence of arsenic is not considered to pose a significant health risk, even after a lifetime consumption of the water. Hence, when setting an MCL it is necessary to better understand and balance the health risks associated with drinking arsenic bearing water against alternative sources of water, the cost and practicality of the treatment and the practical limitations of analytical methods (Waypa et al., 1997).

The treatment of arsenic from drinking water has attracted growing interest due to the negative health effects of drinking arsenic contaminated water as noted above, and to the fact that more stringent standards have been introduced for arsenic in many countries e.g. in the USA and the EU the allowable limit has been reduced from 0.05 mg/L to 0.01 mg/L (Council Directive, 1998; US EPA, 2001). As a result, a lot of research has been carried out with the specific aim of developing cost-effective arsenic removal techniques. Several removal methods have been proposed and adsorption has emerged as one of the most practical methods because it can easily be used in small-scale systems and developing more efficient new adsorbents is possible; a wide range of cost-effective adsorbents are already available or may be developed.

Both arsenite and arsenate have a high affinity for Fe-oxides (Goldberg and Johnston, 2001; Smedley and Kinniburgh, 2002), but the cost of the adsorptive metal removal process is high when pure sorbents (either activated carbon or hydrated Fe- and Al-oxides) are used (Apak et al., 1998). Consequently, the cost of pure adsorbents may be a limitation for many water treatment applications and there is a strong motivation to find cost-efficient alternatives; e.g. red mud, which is used in the present study after neutralising with seawater. Red mud is a fine-textured insoluble residue remaining after the caustic digestion when the Bayer process is used to extract alumina ( $\text{Al}_2\text{O}_3$ ) from bauxite (Chvedov et al., 2001) as shown in Fig.1. In 2003, roughly 22 million tonnes of

**Table 1. World-wide arsenic contaminated areas**

Country and the area	Reference
Argentina	Astolfi et al. (1981)
Bengal Delta (Bangladesh and India)	Das et al. (1995); Mandal et al. (1998); Nickson et al. (1998); Acharyya et al. (1999); Chowdhury et al. (2000); Zang et al. (2001)
Brazil (Iron Quadrangle)	Borba et al. (2000)
Canada (Nova Scotia and Eastern part)	Grantham and Jones (1977); Mucci et al. (2000)
China (Inner Mongolia and Xiangjiang River)	Chunguo and Zihui (1998); Guo et al. (2001)
Chile (Antofagasta and Chiu Chiu)	Borgono and Greiber (1971); Smith et al. (2000); Karcher et al. (1999)
Denmark (Storstrøms, Århus, Fyns, and Vejle)	GEUS (2003)
France (North Mortagne)	Charlet et al. (2001)
Finland (Northern part)	Raisanen et al. (1997)
Germany (Eastern part)	Daus et al. (1998); Ruhland and Jekel (2002)
Ghana (Ashanti region)	Smedley (1996)
Greece (Thessaloniki)	Voutsas et al. (1993)
Hungary	Hodi et al. (1995)
India (Calcutta)	Chatterjee et al. (1993)
Japan (South Chikugo Fukuoka, Fukul, Takatsuki and Kumamoto)	Shimada (1996); Xu et al. (1998)
Mexico (Northern part)	Cebrian et al. (1983); Planer-Friedrich et al. (2001)
Norway	Raisanen et al. (1997)
Sweden	Xu et al. (1991); Lindberg et al. (1997)
Russia (western half of the Russian Kola Peninsula)	Raisanen et al. (1997)
Taiwan (Southwest part)	Tseng (1977); Tseng et al. (2003)
Thailand (Southern part)	Williams et al. (1996)
Turkey (Kütahya and Gediz)	Karayiđit et al. (2000); Çolak et al. (2003)
UK	Lumsdon and Meeusen (2001)
USA (Central Arizona, New Jersey, Lane County (WA), Nevada, Idaho and Utah)	Hathaway and Rubel (1987); Murphy and Aucott (1998); Lewis et al. (1999); Cummings et al. (1999); Foust et al. (2000)
Vietnam (Hanoi Area)	Berg et al. (2001)

alumina were produced worldwide and 10% of this was in Asia. This translates to an annual production of roughly 35 million tonnes of red mud residue worldwide, of which about 3 million are produced in Asia, where the arsenic contamination of drinking water is particularly pronounced (WAO, 2003). In short, red mud is widely available in large quantities, it is rich in Fe- and Al-oxides/hydroxides (Altundoğan et al., 2000), and is expected to have a strong affinity for arsenic.

Currently, red mud is usually dumped in holding ponds or dams, for which large areas are necessary (López et al., 1998), although some refineries dump their red mud in the sea. The red mud dams occupy a large area and can constitute a serious environmental hazard due to the highly caustic nature of the red mud, the fact that it dries exceptionally

slowly, and the fact that wet red mud has a very low physical strength (Hind et al., 1999). The stored red mud can pollute environmental compartments such as soil, surface water and groundwater, and poses serious threats to lives and properties if a red mud reservoir dike bursts (Varnavas and Achilleopoulos, 1995; Zhang et al., 2001). Thus, the reuse of red mud residues is a potentially cost-effective alternative to long term storage in impoundments (McConchie et al., 1999, 2002a, 2002b). Red mud is thus of interest to researchers for many reasons and it has been the subject of many detailed investigations. Of particular interest here is work to ascertain effective uses for seawater neutralised red mud (Bauxsol™) for water treatment, particularly in the arsenic removal field, both to provide economically viable water treatment processes and for environmental protection.

The following statements define the objectives and scope of this study.

**Objectives:** The ultimate objective of this study is to investigate the potential for developing seawater-neutralised red mud (Bauxsol) as a novel adsorbent for arsenic removal from water. Within this objective, the study has four primary aims: (1) to evaluate the possibility of using Bauxsol to remove arsenic from water; (2) to determine whether the arsenic removal capacity of raw Bauxsol can be increased; (3) to develop new granular sorbents from Bauxsol and its activated form for continuous flow experiments; and (4) to get an overview of the capacity of the developed sorbents by comparing them with other arsenic sorbents.

**Delimitation:** The primary focus of the thesis is to elucidate the possibility of using Bauxsol to remove arsenic from water, and to develop new sorbents from Bauxsol to remove arsenic from drinking water in a simple and cost-effective manner. In addition, published literature is surveyed briefly to assess current removal methods and sorbents in comparison to the sorbents used here. The detailed study of the geochemical/mineralogical aspects of the removal process, however, as well as through cost studies or field tests were beyond the scope of the present study.

## 2. Contamination of groundwater with arsenic

High arsenic concentrations have been detected in groundwaters in several parts of the world as shown in Table 1. In this study special attention is devoted to the contamination detected in Bangladesh and the West Bengal area of India because this is by far the most significant area of groundwater arsenic contamination in terms of the number of people affected. In this section arsenic chemistry is briefly introduced followed by an overview of the natural pathways for arsenic entering the groundwater.

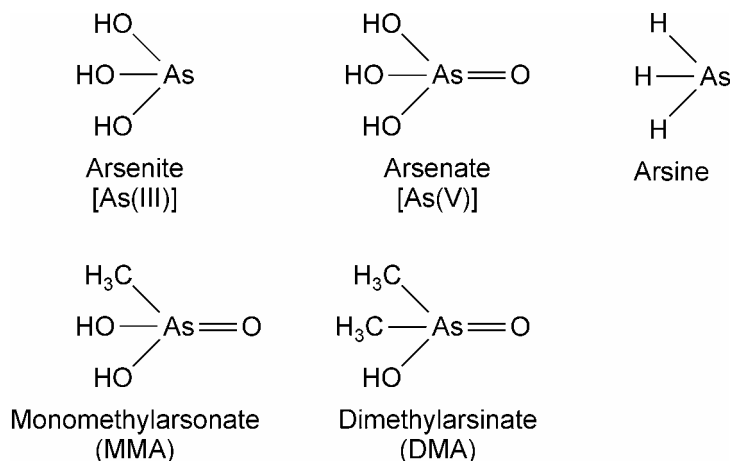
### 2.1. Arsenic chemistry

Arsenic, a metalloid belonging to Group VB of the periodic table below phosphorus, is a common toxic element in the Earth's crust and also present in most natural waters. Arsenic has a rather complicated chemistry, because it can exist in several forms in the environment. Moreover, the mobility, bioavailability and toxicity of arsenic depend on the species in which it exists. For instance, arsenic exists in natural waters primarily as oxyacids of As(V) or arsenate, As(III) or arsenite, and the dominant organic forms exist are monomethylarsonate or MMA, and dimethylarsinate or DMA, where the oxidation state of arsenic in both cases is arsenate (Smedley and Kinniburgh, 2002). In addition, methylated arsenite species can also be present in natural waters (Redman et al., 2002; Thirunavukkarasu et al., 2002) as a result of transformation of arsenical compounds by micro-organisms via in situ biomethylation (some bacteria can replace the hydroxyl groups by methyl groups) or as a result of the application of organoarsenical pesticides (Chatterjee et al., 1993; Waypa et al., 1997; Gallagher et al., 2001; Bissen and Frimmel, 2003). The oxidation of methylated arsenic species to inorganic arsenic species can occur under aerobic conditions (Bissen and Frimmel, 2003). The methylated compounds are roughly 1% as toxic as arsenite and arsenite is about four times more toxic than arsenate (Chatterjee et al., 1993; Viraraghavan et al., 1999; Thirunavukkarasu et al., 2002); insoluble arsenic compounds are less toxic than their soluble counterparts. The higher toxicity of arsenite is attributed to the fact that arsenite ( $\text{AsO}_3^{3-}$ ) exhibits a high affinity for the sulfhydryl groups of amino acids e.g. cysteine, and thereby inactivates a wide range of enzymes in intermediate metabolism (Fendorf et al., 1997).

Arsenite is a common species in reducing environments such as groundwater and exists as uncharged molecules ( $\text{H}_3\text{AsO}_3$ ), whereas arsenate is prevalent in aerated waters and exists as monovalent ( $\text{H}_2\text{AsO}_4^-$ ) or divalent ( $\text{HAsO}_4^{2-}$ ) anions (Ferguson and Gavis, 1972). These forms of arsenic are readily interconverted and may occur together due to the slow oxidation and reduction kinetics (Gupta and Chen, 1978; Edwards, 1994; Karcher et al., 1999; Francesconi and Kuehnelt, 2002). The structures and dissociation constants of major arsenic compounds are given in Figure 1, and Table 2, respectively. In Figure 1, the structure of arsine gas ( $\text{AsH}_3$ ) is also presented because it is the best known of the hydrides of arsenic, and arsenic must be converted to arsine to detect the arsenic by the analytical method used in this study (see chapter 5). Only the inorganic forms of arsenic are considered in this study because organic arsenic compounds do not appear to be particularly important in the overall arsenic cycle (Drever, 1997; Francesconi and Kuehnelt, 2002).

**Table 2. Dissociation constants of  $\text{H}_3\text{AsO}_3$ ,  $\text{H}_3\text{AsO}_4$ , monomethylarsonic acid (MMAA), and dimethylarsinic acid (DMAA) (after Bissen and Frimmel, 2003)**

	$\text{p}K_1$	$\text{p}K_2$	$\text{p}K_3$
$\text{H}_3\text{AsO}_3$	9.2	12.2	13.4
$\text{H}_3\text{AsO}_4$	2.2	7.0	11.5
MMAA	3.6	8.2	-
DMAA	6.3	-	-



**Figure 1. Structures of some environmental arsenic compounds referred to in the text and tables by name or acronym. The compounds are depicted in their fully protonated form (after Francesconi and Kuehnelt, 2002).**

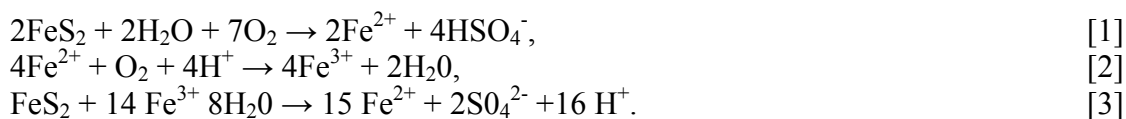
The mobility of arsenic in natural environments is mainly controlled by sorption onto metal-oxides/hydroxides, where the sorption depends mainly on pH conditions, the redox potential and the presence of other oxyanions that compete with arsenic for retention sites (Manning and Goldberg, 1996a; Arai et al., 2001). Arsenite species are more mobile than arsenate in groundwater, because uncharged arsenite is less prone to be sorbed to a mineral surface than the arsenate anions. Arsenate has strong affinity for most metal-oxides/hydroxides and clay minerals, and forms surface complexes, whereas arsenite is more selective although it also has an affinity for Fe-oxides/hydroxides (Inskeep, 2002). Under reducing conditions arsenic compounds bound to Mn- or Fe-oxides/hydroxides are readily mobilised when Fe(III) and Mn(III/IV) are reduced to Fe(II) and to Mn(II), whereas  $\text{As}_2\text{O}_3$  and sulfides are relatively stable (Bissen and Frimmel, 2003). Under oxidising conditions the solubility of arsenic is lower, but arsenic sulphides such as orpiment, realgar and arsenopyrite tend to oxidise and release arsenic.

## 2.2. Arsenic in groundwater

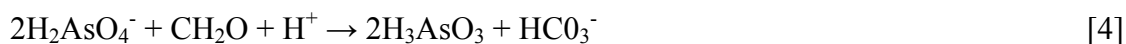
In Bangladesh and the West Bengal area of India, the presence of elevated arsenic concentrations in groundwater is believed to be natural, as no anthropogenic source is likely to cause such a widespread arsenic contamination (Mandal et al., 1998). During

the 1970s, in the context of very high occurrences of diarrhoeal diseases, bacteriological quality received priority as a criterion for drinking water supply, and the use of pathogenic microorganism-free groundwater was strongly encouraged by several international institutions, including the World Bank. This led almost 97% of the rural people to use tube wells in Bangladesh. Unfortunately, in recent years the presence of arsenic in excess of acceptable limits has been found in groundwaters in many parts of Bangladesh and West Bengal, and millions of people have shown symptoms of being poisoned by arsenic.

Although it is well established that sorption and desorption are major reaction mechanisms controlling the fate of arsenic in soil and groundwater, there is no general consensus about what mechanisms are responsible for these elevated arsenic concentrations in the Bay of Bengal groundwater (Goldberg and Johnston, 2001). Two principal hypotheses about the natural genesis of arsenic in the groundwater are mentioned in the literature. Previously, it was believed that high arsenic concentrations in the groundwater were related to the oxidative decomposition of arsenopyrite (FeAsS), the most abundant arsenic containing mineral (Francesconi and Kuehnelt, 2002), or other arsenic containing minerals in subsurface sediments due to excessive groundwater withdrawal (Das et al., 1995). Increasing recharge with water containing dissolved oxygen could result in the release of additional dissolved arsenic, as occurs in some acid sulfate soils, (Dhar et al., 1997). The decomposition of arsenic rich pyrite (FeS<sub>2</sub>), defined with the following reactions (Mandal et al., 1998), can also release arsenic into groundwater.



However, present data suggest that when anoxic conditions are dominant the reduction of arseniferous iron hydroxides leads to arsenic release to the groundwater (Nickson et al., 1998, 2000; Chowdhury et al., 2000) and it is postulated that most of the arsenic is released as a result of microbial dissolution of these oxides (Xu et al., 1998; Mandal et al., 1998). Furthermore, low pH conditions in near-surface waters could also cause dissolution of metal hydroxides that would otherwise bind inorganic arsenic by co-precipitation (Xu et al., 1998). The role of arsenic reducing bacteria on the mobility of arsenic is highlighted by Cummings et al. (1999). They suggest that some organisms, i.e. *Geospirillum barnesii* strain SES-3, may reduce both Fe(III) and arsenate, which in turn promote rapid arsenic solubilization. The reduction process converts precipitated and adsorbed arsenate into more soluble arsenite. Microbiologically induced reduction may be defined in the following pathway (Bhattacharyya et al., 2003):



Other studies suggest that neither of the above mentioned mechanisms alone is sufficient to explain the concentration and distribution of arsenic in the groundwater and that both mechanisms are involved (Acharyya et al., 1999).



### 3. Comparing arsenic removal technologies

This section provides an overview for the most commonly used arsenic removal methods and presents some basic criteria to consider when comparing these methods; the main advantages and disadvantages of each method are also listed. Various treatment technologies have been proposed in the literature for the removal of arsenic from water. Readily available literature on arsenic removal methods includes conservative treatment processes (e.g. coagulation), softening and iron-manganese oxidation, co-precipitation, membrane processes, ion exchange and adsorption processes, in-situ immobilization, and biological oxidation of iron and manganese. Although many of these technologies are well developed (with some already implemented at the community level), they are often considered expensive and consequently, new cost effective technologies applicable at small scales remain in demand.

When choosing a removal method, it is necessary to consider the final desired concentration as well as the associated costs and the feasibility of monitoring this goal. The natural distribution of inorganic arsenic species i.e. arsenite and arsenate in water influences both the treatment strategy and the removal efficiency (Gallagher et al., 2001). The anionic characteristics of arsenate promote its removal, whereas the neutral characteristics of arsenite limit its removal efficiency in conventionally applied physicochemical treatment methods at near neutral pH values (McNeill and Edwards, 1997; Genç-Fuhrman et al., 2004a). Thus, if arsenic is present wholly or partly in arsenite form, most of the arsenic removal methods require a pre-oxidation step to oxidise arsenite to arsenate for an efficient arsenic removal. In addition, the form of the arsenic present in the water (particulate/colloidal or dissolved) may also be important for the treatment process in terms of the process selection and expected performance (Wilkie and Hering, 1996; Brandhuber and Amy, 2001). In surface waters the fraction of particulate arsenic may consistently contribute to the total arsenic, indicating the presence of complex arsenic species besides arsenic and arsenous acid (McNeill and Edwards, 1995). However in groundwater, arsenic is found to be mostly in dissolved forms (<3.000 Daltons) (Wang et al., 2002), but in well water samples the particulate arsenic concentration can also be as high as 70% of the total arsenic (Chen et al., 1999; Le, 2002). If the particulate arsenic fraction is high enough, filtration alone may be sufficient to meet the arsenic concentration limits for potable water (Chen et al., 1999).

When evaluating the existing technologies, the decision making process usually starts with determining the goals and the respective criteria relevant for the evaluation (Ruhland and Jekel, 2002). Although evaluating several alternatives may look challenging, Ruhland and Jekel (2002) suggest the methodology of multiple criteria decision making (MCDM) for describing the general requirements. It is beyond the scope of this study to present details on the MCDM method, but more information on application of the method can be found in the literature (e.g. Ruhland and Jekel, 2002). Here, it is proposed that for an appropriate arsenic removal technique the following requirements should be fulfilled:

- i) Water quality

- a. The selected method must be effective enough to meet the required water quality standards for arsenic.
  - b. The necessity of meeting other water quality standards besides arsenic is highlighted. If the applied method is not capable of meeting the standards for other water contaminants or if the technology itself is a source of unwanted contaminants to the water, a secondary treatment may be needed, hence increasing the overall cost.
  - c. The selected method must perform well in the combined presence of potentially competing ions such as phosphate, silicate, sulfate and bicarbonate, and the method should be tested using natural water samples.
- ii) Economy
  - a. The expected cost of the method in terms of set-up, operation and maintenance should be affordable.
- iii) Operation & Maintenance
  - a. Simple operational and maintenance requirements should be preferred in addition to minimal energy requirements.
  - b. Optimum pH range for the removal needs to be taken into account, as changing the pH during, before or after the treatment may not be practical. Moreover, if the method is effective within a small range of pH it may be difficult to maintain this pH throughout the removal.
- iv) Safety & Reliability
  - a. Operation of the process should be safe, reliable and robust.
  - b. Storage and handling of any required chemicals should be addressed, including the associated costs.
  - c. The method should preferably be effective in removing both arsenite and arsenate species.
- v) Social acceptance
  - a. The likely acceptance of the method by local residents should be evaluated.
- vi) Environmental effects
  - a. If other pollutants are produced as a result of the treatment such as wastewater and toxic sludge, their treatment should be addressed.
  - b. Occupational health (hazard potential of the utilised chemicals) should be considered (Ruhland and Jekel, 2002).
- vii) The process must also be evaluated by answering the following questions:
  - a. Can the process meet new stringent standards?
  - b. If a sorption process is applied, is the regeneration of the sorbent possible and favourable, and is it possible to address the safe handling and disposal of the spent regenerate?

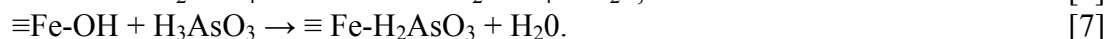
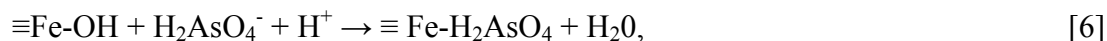
In the following sections the main arsenic removal methods and their process characteristics are reported, and those most widely used are accompanied by a brief description of their main advantages and disadvantages.

### **3.1. Oxidation**

Most of the arsenic removal technologies perform better when removing anionic arsenate than uncharged arsenite at circum-neutral pH values. Therefore, a pre-oxidation step before applying the main removal process is commonly included as the first treatment step towards arsenic-free drinking water. Although arsenite should be readily oxidised to arsenate by dissolved oxygen, it persists in aerated waters due to slow oxidation reaction kinetics (Driehaus et al., 1995). Chlorine, ozone, potassium permanganate, manganese oxides and hydrogen peroxide can be used to accelerate oxidation (Kartinen and Martin, 1995; Driehaus et al., 1995) and promising results have been reported using UV light for the oxidation at the presence of dissolved iron compounds (Zaw and Emett, 2002). All oxidants have their advantages and disadvantages that should be taken into account when choosing the one to be used. For instance, although high oxidation efficiency is obtained using chlorine, the possibility of producing elevated concentrations of unwanted disinfection by-products with organic matter, and the release of taste and odour compounds from algal cells should be considered (Gregor, 2001). Potassium permanganate, on the other hand, produces no harmful by-products, but may produce colour in the water and cause filtration problems later in the treatment plant (Borho and Wilderer, 1996). It should be noted that oxidation alone cannot serve as a sufficient technology for arsenic removal, though it may well be employed as a pre-treatment step to increase the efficiency of the main removal method. Biological oxidation of iron and manganese may be inexpensive, but is not yet fully established.

### **3.2. Chemical precipitation through coagulation-filtration**

Chemical precipitation through coagulation filtration includes alum coagulation, iron coagulation and lime softening. Coagulants are those substances that are capable of removing colloidal impurities from water, and coagulation is the process by which such removal is brought about (Pande et al., 1997). Entrapment during coagulation removes the particulate arsenic (Gregor, 2001), but mechanisms other than entrapment are required to remove soluble arsenic. Co-precipitation occurs when an inorganic contaminant (e.g. arsenic) forms an insoluble complex (e.g. metal hydroxide flocs) with the coagulant. This may occur via adsorption, inclusion or occlusion (Edwards, 1994). Aluminum or ferric chlorides/sulfates can be added as coagulants, and following their addition the relevant amorphous aluminum hydroxide ( $\text{Al}(\text{OH})_3(\text{am})$ ) or ferric hydroxide ( $\text{Fe}(\text{OH})_3(\text{am})$ ) is precipitated (Cheng et al., 1994; Hering et al., 1997). Moreover, the addition of aluminum or iron coagulants facilitates the conversion of soluble inorganic arsenic species into insoluble products by precipitation, co-precipitation or adsorption. The formation of these insoluble products facilitates their subsequent removal from the water by means of sedimentation and filtration processes (McNeill and Edwards, 1995; Sancha, 2000). The following reactions illustrate the arsenate, [6], and arsenite, [7], adsorption involved in the process (after Edwards, 1994):



These reactions can be used to represent the arsenate and arsenite adsorption in the processes, respectively. Here,  $\equiv\text{Fe-OH}$  is a hydroxide surface site. At high coagulant dosages the adsorption of inorganic arsenic to precipitated metal hydroxide solids takes place, but entrapment of adsorbed contaminants in the interior of the growing particle and solid-solution formation may also take place, especially at low coagulant dosages (Hering et al., 1997).

Lime treatment is similar to coagulation with trivalent metal salts but instead of metal hydroxides, hydrated lime ( $\text{Ca(OH)}_2$ ) or  $\text{Mg(OH)}_2$  solids form. Here the main arsenic removal mechanisms involve calcite precipitation (less effective) and sorption to  $\text{Mg(OH)}_2$  solids (more effective) (McNeill and Edwards, 1995). The process, however, can not serve as a major arsenic removal mechanism due to the low removal efficiencies, and unfavourable operating conditions (very high pH and chemical dose rates are required).

Previous studies have concluded that arsenate is more effectively removed than arsenite when using coagulation, thus a pre-oxidation step to oxidise arsenite to arsenate is beneficial (Hering et al., 1997). In addition, coagulation also has other limitations. In particular, coagulation has the disadvantage of high daily toxic sludge production. The flocs are usually dominated by fine colloidal particles and it can be very difficult to dewater them, resulting in large volumes of residual wet sludge that are difficult to manage (Xu et al., 1998). Consequently, the method cannot be readily applied to small and intermittent flows (Kartinen and Martin, 1995; Viraraghavan et al., 1996). Furthermore, if the water contains large amounts of phosphate and fluoride along with the arsenic, optimum conditions for arsenic removal may not be compatible with conditions favouring the removal of these other anions (Johnston and Heijnen, 2001).

The costs associated with this method include coagulation chemicals, pH adjustment before and after treatment, and sludge residue management. The advantages of this method (Cheng et al., 1994; McNeill and Edwards, 1995; Scott et al., 1995; Hering et al., 1996, 1997; Pande et al., 1997; Gregor, 2001; Holm, 2002) can be summarised as:

- The method is already in use in many water treatment facilities.
- No monitoring of a breakthrough point is required (though it may still be used to confirm the arsenic removal).
- The chemicals required are simple and low cost.
- The process has been tested in full scale applications.
- Arsenic removal efficiency may be independent of the initial arsenic concentration.

Whereas the associated disadvantages are:

- The procedure is effective only over a narrow pH range and coagulant dosage.
- Disposal of arsenic contaminated coagulant sludge (toxic) poses problems.
- The presence of competing ions needs to be considered.
- Safe storage of chemicals needs to be addressed.

- Arsenite needs to be oxidised to arsenate for effective removal.
- Disinfection is needed (but chlorination may have some adverse effects).
- Secondary treatment is necessary to meet the arsenic standard in lime treatment systems.

### **3.3. Adsorption, surface precipitation and ion exchange**

Adsorption systems are becoming more popular, especially in small scale treatment systems such as at the household level (Thirunavukkarasu et al., 2003). This is important in countries like Bangladesh, where the water system is not centralised and individual households or small groups are served by their own well (Mamtaz and Bache, 2001). Adsorption is a mass transfer process, which refers to the accumulation of sorbates at the liquid/solid interface. Arsenic can be sorbed to several sorbents. Some of the widely used arsenic sorbents are later compared in terms of their adsorption capacity and discussed in Chapter 5. Adsorption data in the literature cannot, however, be easily compared with one another due to large reported (or not reported) differences in experimental procedures and conditions (Xu et al., 1991). Thus, the comparison is made by simply providing the reported experimental conditions along with the adsorption capacity data.

One of the most common methods for arsenic removal from water is the precipitation of arsenic as calcium arsenates or ferric arsenates at an optimum pH range, which varies for each and exhibits solubility minima (Bothe and Brown, 1999). In these precipitation processes, dissolved ions in a solution form an insoluble solid via a chemical reaction e.g. naturally occurring dissolved iron forms a precipitate when it is exposed to air.

Although ion exchange resins can be used to remove arsenic from water over a wide pH range, different resins have different exchange capacities; e.g. conventional sulfate resins are particularly suited for arsenate removal, but uncharged arsenite cannot be removed (Johnston and Heijnen, 2001). In addition, another concern is that competing anions, especially sulfate, obstruct arsenic removal because most of the resins are more selective towards sulfate.

The associated costs of these methods include pH adjustment, operation and maintenance costs, the cost of the sorbent itself, and safe handling of the spent sorbent (disposal or regeneration). The advantages of this method (Kartinen and Martin, 1995; Manning and Goldberg, 1997; Bajpai et al., 1999; Chen et al., 1999; Chwirka et al., 2000; O'Reilly et al., 2001; Korngold et al., 2001) can be summarised as:

- User friendly at the household level (e.g. chemical addition may not be required).
- These methods may be cheap depending on the adsorbent used.
- Several low cost new adsorbents are available, or there are endless possibilities to develop new ones.
- There is no daily sludge production problem.
- The efficiency of the ion exchange process is less sensitive to the pH of the water.

Whereas the main disadvantages are:

- Periodic regeneration of the sorbent may be required depending on the sorbent.
- Requires monitoring of breakthrough or filter use.
- These methods may be expensive depending on the sorbent.
- pH adjustment before and after the process may be necessary.
- Chemical handling may be difficult for some small systems.
- Pre-oxidation is generally required, but the oxidants may harm the ion exchange resin.
- Ion exchange efficiency will be limited by competition with other anions (e.g. sulfate, phosphate, nitrate etc.) and pre-treatment may be necessary.
- Bicarbonate removal during the ion exchange process reduces the pH and increases the corrosiveness of the treated water.
- If ion exchange is used beyond the point of sulfate exhaustion, the removed arsenic may be released back into the treated water.

### **3.4. Membrane technologies**

Membrane units include coagulation/microfiltration, reverse osmosis (e.g. nanofiltration and ultrafiltration) and electrodialysis and uses special filter media that physically retain the impurities present in water. When arsenic contaminated water passes through the media, all kinds of impurities, including arsenic, are removed from the water. The process is expected to have high arsenic removal efficiency as a result of the small molecular weight of dissolved arsenic species (<150 Daltons). Furthermore, when the membrane is slightly negatively charged, it is advantageous for the removal of arsenic from water (Brandhuber and Amy, 2001). Source water quality and the effluent concentration to be reached are important design parameters. If the water is free of suspended solids before the membrane treatment, then the process can be very effective, but high capital and operational costs are major concerns. The costs associated of these methods include the cost of membrane unit construction (e.g. pumps, etc.) as well as additional treatment costs (especially at high initial arsenic concentrations). The advantages of membrane technologies (Kartinen and Martin, 1995; Waypa et al., 1997; Vrijenhoek and Waypa, 2000; Johnston and Heijnen, 2001; Sato et al., 2002) can be summarised as:

- Membrane technologies can be very effective at the household level.
- Pre-oxidation may not be necessary.
- The process efficiency is independent of pH within the pH 4-8 range.
- The process requires little space.
- Well defined high removal efficiency is superior to other methods.
- The process functions without any chemical addition.
- No solid waste produced as a result of the treatment.
- The process is capable of removal of other dissolved contaminants, if any.
- Disposal of used membranes is simple.

Whereas the associated disadvantages are:

- High running and investment cost is a limitation.

- The method usually requires a power source that may not always be available (e.g. in the Bangladesh delta area) or may be unreliable.
- Pressure, flow rate, and pH needs to be controlled.
- Guideline values are not met for high initial arsenic concentrations.
- Loss of influent water (20- 25%) may be a concern in water-scarce regions.
- Pre-treatment of the water may be necessary e.g. for removing salts.
- Re-adjustment of water quality after the treatment may be required.
- More highly contaminated wastewater is produced as a result of the process.
- Membrane technologies work better for arsenate, but the membrane may not withstand the oxidant used to oxidise any arsenite.
- For long term use of these methods fouling must be considered.

### **3.5. Other processes**

In addition to the widely used methods discussed above, some other methods are also reported in the literature including microbial processes, *in-situ* immobilization, point of use units and taking advantage of naturally occurring iron.

#### **3.5.1. Microbial processes**

Several bacteria are capable of oxidising arsenite to arsenate thereby eliminating the need for the use of oxidants in other treatments. Furthermore, during biological treatment, the microorganisms can not only change arsenic speciation, but can also remove arsenic at various conditions of temperature, pH, etc. The action of sulfate reducing bacteria is reported by Jong and Parry (2003) to decrease the soluble arsenic concentration, but the exact removal mechanism involved is not yet clear.

#### **3.5.2. *In-situ* immobilisation**

The cost of *in-situ* immobilisation includes both the cost of the chemical used (e.g. potassium permanganate or zero valent iron) and the cost of applying the chemical where it can interact with the arsenic contaminated water. The advantage of the method is that since it is *in-situ* no concentrations of waste are produced. Unfortunately, only a few studies have examined *in-situ* immobilisation, and the effect on the environment is not well established (Matthess, 1981; Rott and Friedle, 2000).

#### **3.5.3. Point-of-use units**

With point-of-use units that make use of one or more of the techniques discussed above, the costs include those of the sorbent as well as costs associated with monitoring and maintenance. The method can be reliable and easy to handle and may be cost-effective, particularly where electricity is not required (Fox, 1989; Meng et al., 2001). However, regeneration of the sorbent and monitoring and maintenance are required and may not be easily undertaken in remote or under developed areas where arsenic contamination in

drinking water is a problem. This method can only be a temporary solution (Bissen and Frimmel, 2003a).

#### **3.5.4. Using naturally occurring iron**

In Bangladesh and India the groundwater often contains excess iron in addition to the arsenic and this situation may be taken advantage of to remove arsenic. The naturally occurring iron is present in the groundwater as the dissolved ferrous iron and under appropriate redox and pH conditions this ferrous iron readily oxidises to form a fresh ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) precipitate that will remove arsenic. High arsenic removal efficiencies may be achieved where iron concentrations are sufficiently high (Mamtaz and Bache, 2001). Although the method looks promising and may be useful in some areas, it has a major limitation because there is no clear correlation between the iron and the arsenic concentrations in the groundwater. However, the method could be applied effectively by aerating extracted groundwater and removing any arsenic contaminated ferruginous precipitate by simple filtration using a sand filter. Even where there is insufficient iron in the water, this method could be used to remove some of the arsenic before final water treatment using one of the other methods, thereby reducing the costs involved in the final treatment.



## 4. Red mud and sorbents used in the study

In this section, red mud and sorbents derived from red mud to use in batch and column experiments are introduced. Moreover, a simple schema is presented to provide an overview of the used sorbents.

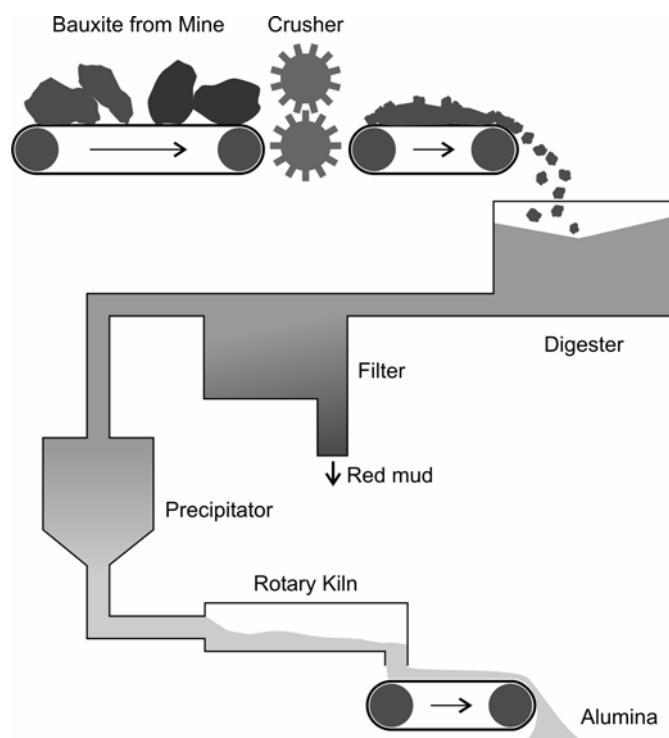
### 4. 1. Red mud

Red mud is the caustic residue resulting from the production of alumina by the Bayer process, which is presented in Figure 2. In Bayer process, between 1 and 2 tonnes (dry weight) of red mud remains for every tonne of alumina produced (McConchie et al., 1999). Consequently, millions of tonnes of red mud are available world-wide and need to be disposed of (Singh et al., 1997). The environmental impacts of the red mud disposal are summarised by Li (1998):

- Leakage of the alkaline supernatant and pore water into the ground leads to contamination of both the soil and water resources.
- Spillage of red mud due to overflow or failure of containment dams (as a result of heavy rain) poses threats to natural water resources and habitation in surrounding areas.
- Air may be polluted by red mud dust, generated from any dried surface of a containment reservoir.
- A vast area of land is consumed for the mud disposal and containment, which reduces the availability of usable land.
- Aesthetic damage to the landscape occurs, because red mud takes years to dry up before reclamation.

It is important to note that several of these impact are only true for unneutralised red mud, and if the red mud is neutralised it is no longer caustic (McConchie et al., 2002a); and that all red mud in this study is wholly or partly neutralised with seawater. Individual red muds may differ widely in composition depending on the origin of bauxite and the operational procedures used at each refinery, some discussion on the relationship between bauxite source and red mud composition for different refineries has been reported elsewhere (Hajela et al., 1989). The mineralogical and chemical composition of red mud has also been previously studied (Altundoğan et al., 2000). Accordingly, red mud is comprised of a number of potential adsorbents and flocculants, and contains abundant finely divided Fe- (giving the red colour), Al- and Ti-oxides/oxyhydroxides (along with other minor components). The organic matter content of red mud is similar to that of bauxite (i.e. usually less than 0.1%; Li, 1998). In relation to arsenic removal, the combined presence of ferric and aluminum compounds is expected to be particularly effective (Apak and Ünseren, 1987), based on studies where Fe- and Al-oxides/hydroxides are both effectively used as arsenic sorbents (Manning and Goldberg, 1997).

Several studies have been reported in the literature, where red mud is used for water and wastewater treatment via sorption. The sorption of both cations and anions onto red mud and its conditioned forms has been successfully carried out. Here, several of these



**Figure 2. Red mud generation in the Bayer process (after WAO, 2003).**

studies are compiled and reported in Table 3 in terms of their adsorption capacity (using the Langmuir constants) at a given pH for the reader's convenience. It can be seen from Table 3 that red mud is capable of adsorbing several contaminants e.g. heavy metal cations (Apak et al., 1998; Lombi et al., 2002), phosphate (Shiao and Akashi, 1977; Koumanova et al., 1997; Pradhan et al., 1998), arsenic (Altundoğan et al., 2000, 2002) and bacteria (Ho et al., 1991), due to its high Al-, Fe-, Ti- and Ca-oxide/hydroxide content. It can also be seen from Table 3 that red mud is in general more effective for cation removal. Besides the solid form of red mud, suspensions of red mud are also used for arsenic removal by co-precipitation with aluminum hydroxide, where promising results are reported (Altundoğan and Tümen, 2003). Furthermore, the recovery of some of the minerals present in red mud has also been reported (Erçağ and Epak, 1997; Çengelöğlu et al., 2001).

#### **4.2. Sorbents used in the study**

Five different sorbents, namely seawater-neutralised red mud (Bauxsol), acid treated Bauxsol (ATB), activated Bauxsol (AB), Bauxsol coated sand (BCS), and AB coated sand (ABCS) are used in batch or column experiments in this study. Bauxsol and AB with added ferric or aluminum sulfate were also tested in the batch experiments. A simple sorbent production scheme is presented in Genç-Fuhrman et al. (2004c), and is represented in Fig. 3 (after modification to further include ferric and aluminum sulfate added Bauxsol or AB). Details on the preparation of each sorbent can be found in Genç et al. (2003) and Genç-Fuhrman et al. (2004, 2004b).

**Table 3. Utilisation of red mud as an adsorbent**

Adsorbate	Langmuir Constants		pH	Reference
	$Q_0^1$ , mg/g	$b^1$ , L/mg		
Cr(VI)	1598.48	0.005	5.2	Pradhan et al. (1999)
Pb(II)	173.47	0.004	5.0	Apak et al. (1998a)
Cd <sup>2+</sup>	108.58	0.008	5.0	Apak et al. (1998a)
PO <sub>4</sub> <sup>3-</sup>	71.25	0.09	5.2	Pradhan et al. (1998)
Cu <sup>2+</sup>	66.68	0.02	5.5	Apak et al. (1998a)
P <sup>5+</sup>	58.11	0.01	7.0	López et al. (1998)
Cu <sup>2+</sup>	19.72	20.29	7.0	López et al. (1998)
Zn <sup>2+</sup>	12.59	119.5	7.0	López et al. (1998)
Ni <sup>2+</sup>	10.95	71.93	7.0	López et al. (1998)
Cd <sup>2+</sup>	10.57	263.4	7.0	López et al. (1998)
Congo red	4.05	0.04	7.3	Namasivayam and Arasi (1997)
Acid violet	1.37	0.07	4.1	Namasivayam et al. (2001)
As(V) <sup>2</sup>	0.94	2.77	3.5	Altundoğan et al. (2002)
As(III) <sup>2</sup>	0.89	0.97	7.3	Altundoğan et al. (2002)
As(III)	0.67	0.33	9.5	Altundoğan et al. (2000)
As(V)	0.52	1.64	3.2	Altundoğan et al. (2000)

<sup>1</sup>  $Q_0$  and  $b$  are calculated using the Langmuir equation (i.e. [9]).  $Q_0$  is the adsorption maximum, and  $b$  is the Langmuir constant related to the energy of the adsorption. <sup>2</sup> Activated red mud is used as an adsorbent.

**Table 4. Chemical composition of Bauxsol and activated Bauxsol (AB) (Genç-Fuhrman et al., 2004b)**

Chemical composition					
Constituent	% (w/w)		Constituent	% (w/w)	
	Bauxsol	AB		Bauxsol	AB
Fe <sub>2</sub> O <sub>3</sub>	34.05	46.55	Na <sub>2</sub> O	2.74	0.5
Al <sub>2</sub> O <sub>3</sub>	25.45	26.51	MgO	1.86	0.5
SiO <sub>2</sub>	17.06	17.4	K <sub>2</sub> O	0.20	0.4
TiO <sub>2</sub>	4.90	6.9	P <sub>2</sub> O <sub>5</sub>	0.15	0.4
CaO	3.69	0.7	MnO	0.04	0.1
Misc.	9.86	-			

#### 4.2.1. Seawater-neutralised red mud (Bauxsol)

Untreated red mud is highly caustic (the pH is usually >13.0), due to the presence of residual NaOH during bauxite digestion and the formation of some Na<sub>2</sub>CO<sub>3</sub>. This high alkalinity is environmentally hazardous, and therefore red mud needs to be neutralised before it can be used for water treatment; it also needs to be neutralised if it is to be stored safely or regenerated. Several methods for the neutralisation of red mud have been previously reported e.g. with the addition of gypsum or acid (López et al., 1998) or using either Ca- and Mg-rich brines or water with added CaCl<sub>2</sub> and MgCl<sub>2</sub> (McConchie et al., 2002a). The red mud used in this study has been seawater-neutralised

(McConchie et al., 1999, 2002a), as the seawater-neutralisation is both cheap and simple. The composition and mineralogy of major components in the Bauxsol used in this study is reported in Genç et al. (2003), and additional compositional and mineralogical details can be found elsewhere (McConchie et al., 1999; Clark, 2000). The chemistry of the seawater-neutralisation is described in detail by McConchie et al. (1999). Consequently, during the reaction with seawater hydroxyl ions in the red mud are neutralised largely by reaction with magnesium to form brucite, hydrocalumite, hydrotalcite and p-aluminohydrocalcite. Carbonate ions also react with calcium in the seawater to form calcite and aragonite.

#### **4.2.2. Acid treated Bauxsol (ATB) and activated Bauxsol (AB)**

Acid treatment, and acid and heat treatment of Bauxsol is carried out as suggested by Pratt and Christoverson (1982) to improve the sorptive capacity of Bauxsol. During acid treatment with HCl, sodium compounds that adversely affect the arsenic adsorption are removed (Shiao and Akashi, 1977; Altundoğan et al., 2002; Genç-Fuhrman et al., 2004). Here, the reason hydrochloric acid (HCl) is selected for the acid treatment over sulphuric acid ( $\text{H}_2\text{SO}_4$ ) is that HCl can yield significantly more  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  and soluble hydroxo-complexes than can  $\text{H}_2\text{SO}_4$  (Apak and Ünseren, 1987). Moreover, the addition of sulfate to the system is a disadvantage, as sulfate diminishes the arsenate removal (Genç and Tjell, 2003; Genç et al., 2003).

When the sorptive capacities of Bauxsol and the sorbents obtained from acid treatment and the combined acid and heat treatment are compared, it is found that the combined acid and heat treated Bauxsol, activated Bauxsol (AB), performs the best. This suggests the further improvement of the sorptive capacity during the heat treatment. The chemical and mineralogical characteristics of Bauxsol and AB are presented in Table 4, where it is evident that the Fe- and Al-oxide content of AB is greater than that of Bauxsol. After the treatment, a roughly 300% increase in surface area and cation exchange capacity is observed for AB (Genç-Fuhrman et al., 2004), which may partly account for the increase in the adsorption capacity. The removal of sodium could also account in part for the increased surface area (Pratt and Christoverson, 1982). Most importantly, the arsenate removal capacity is significantly increased after the treatment (Genç-Fuhrman et al., 2004). It is however, important to note that although the surface area of AB is roughly two times greater than that of acid treated Bauxsol (ATB), the arsenate removal obtained using AB and ATB are 100% and 95%, respectively. This observation may reflect the fact that micro pores, which primarily contribute to the surface area, did not actively take part in the adsorption (Elizalde-González et al., 2001), as the observed difference for the arsenate removal is less than the relative difference in surface area. Another difference between the Bauxsol and AB, that could affect arsenate sorption, is that unlike slightly alkaline Bauxsol, AB has a near-neutral reaction pH when suspended in water.

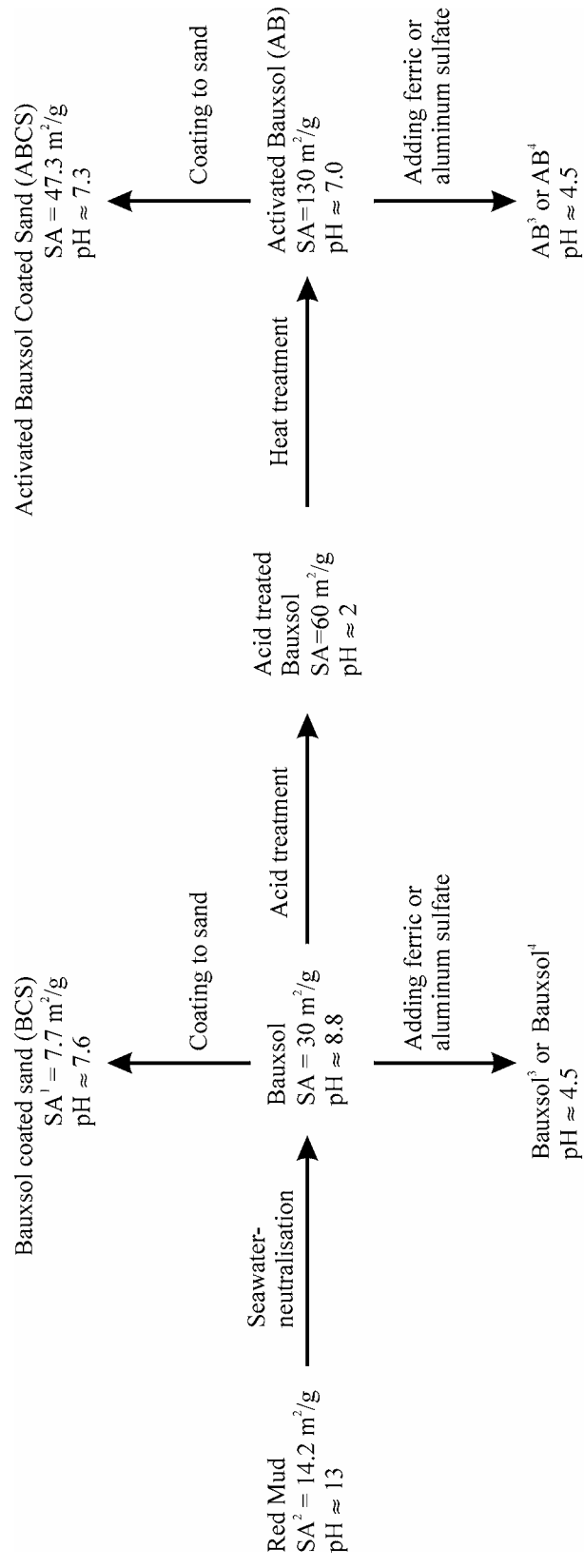
#### **4.2.3. Ferric or aluminum sulfate added Bauxsol and AB**

In addition to applying activation methods described above, another attempt was made to increase the arsenic removal efficiency by adding ferric sulfate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ ) or

aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ) to the Bauxsol and AB. As expected, the addition of these reagents reduced the pH to 4.5, due to hydrolysis reactions (e.g.  $\text{Fe(III)} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3$ ), and increased the availability of potentially arsenic-binding Al and Fe hydroxides (Sutherland, et al., 2002). Nevertheless, the addition of these reagents did not enhance arsenic removal and in fact, their addition reduced arsenate adsorption slightly. Aluminum sulfate most significantly suppressed the removal, whereas the suppressive effect of ferric sulfate was minor. Later experiments were repeated using AB with analogous results observed for AB following the addition of ferric or aluminum sulfate (Genç-Fuhrman et al., 2004). Several reasons are postulated to explain the observed data, including sulfate competition for the available adsorption sites, formation of watery gels covering the surface, and unfavourable pH conditions (Genç-Fuhrman et al., 2004). With the benefit of hindsight, it seems likely that better arsenic removal would have been obtained by using ferric or aluminum chloride instead of ferric or aluminum sulfate; because both sulfate competition and gel formation would have been greatly reduced. However, Ruhland and Jekel (2002) report that the ferric chloride backwash sludge may be less desirable because ferric sulfate sludge has better characteristics for sedimentation and thickening. Clearly, further investigations will be required to resolve these questions.

#### **4.2.4. Bauxsol coated sand (BCS) and AB coated sand (ABCS)**

Because Bauxsol and AB contain very fine particles, they are not suitable for use as filter mediums in fixed bed column tests where they may cause severe clogging. Thus, Bauxsol and AB are coated to sand as described in Genç-Fuhrman et al. (2004c) and used as a filter medium in column tests, as well as in batch tests to obtain the adsorption capacity.



<sup>1</sup> Surface area

<sup>2</sup> From Apak et al. (1998)

<sup>3</sup> Bauxsol or AB with ferric sulfate

<sup>4</sup> Bauxsol or AB with aluminum sulfate

**Figure 3. Preparation of seawater-neutralised red mud (Bauxsol), acid treated Bauxsol (ATB), Activated Bauxsol (AB), Bauxsol coated sand (BCS), AB coated sand (ABCS), and ferric or aluminum sulfate added Bauxsol and AB.**

**Table 5. Analytical methods for the determination of total arsenic concentrations (summarised from Goessler and Kuehnelt, 2002)**

<b>A. Spectrophotometric Methods</b>	<b>B. Electrochemical Techniques</b>	<b>C. Atomic Absorption Spectrometry</b>	<b>D. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)</b>	<b>E. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)</b>	<b>F. Hydride Generation Techniques (HG)</b>
<p>i) Marsh test (not a spectrophotometric method, only to determine the presence of arsenic)</p> <p>ii) Molybdenum blue method (only arsenate can be measured, method interferes with the presence of phosphate and silicate)</p> <p>iii) Silver diethyldithiocarbamate method (commonly used for determination of arsenic in water)</p>	<p>Not commonly used due to severe interferences, Can be used to measure As(III) in the presence of As(V) (Khan et al., 2000).</p>	<p>i) FAAS<sup>1</sup> (serious interferences and high detection limit (1 mg/L))</p> <p>ii) GFAAS<sup>2</sup> (widely used but matrix modifiers are needed)</p>	<p>High detection limit (30 µg/L), Suffers from interferences, Frequently coupled with hydride generation system to overcome interference and high detection limit.</p>	<p>Superior to other methods due to very low detection limit and multi-element capability.</p>	<p>Widely used and can be connected to various detection systems, Arsenic speciation is possible with a pH control of hydride generation reaction.</p>

<sup>1</sup> Flame atomic absorption spectrometry. <sup>2</sup> Graphite furnace atomic absorption spectrometry

## 5. Arsenic removal using Bauxsol or activated Bauxsol in batch system

Batch adsorption experiments are commonly applied in the literature to study arsenic adsorption, as well as to provide data on the adsorption kinetics and other adsorption characteristics. Batch tests are run here using the developed sorbents to elucidate the sorptive characteristics. Results are presented in the following sequence: first the experimental set-up in terms of the arsenic measurements is described, and second the main findings from the batch tests are presented. Note that this section is limited to assessing the batch test data; data obtained from column studies are presented in a later section.

### 5.1. Arsenic measurements

Several analytical methods are available for arsenic measurement in water as presented in Table 5, but for this study hydride generation atomic absorption spectrometry (HGAAS) was selected as the most suitable method for the arsenic concentrations to be used and for the concentrations of potentially interfering species likely to be encountered. HGAAS is one of the most widely used and well established techniques for arsenic determination in water (Manning and Mortens, 1997) and it has been found to be very accurate and free from major interferences (Thompson and Thomerson, 1974). In the first part of the study (Genç et al., 2003) a batch system is used for arsenic detection. Later, due to practical difficulties, the atomic absorption spectrophotometer (AAS Perkin Elmer 5000) was connected to an online arsine generation system (MHS-10) for the remainder of the study. Details of the arsenic measurements throughout the study are presented in Genç et al. (2003) and Genç-Fuhrman et al. (2004). The operating conditions for the HGAAS used in this study are listed in Table 6.

One of the most commonly selected methods to separate arsenic from potentially interfering elements and to avoid matrix influence involves volatilization as arsine (see Fig. 1 for the chemical structure of arsine) in a hydride generation unit using  $\text{NaBH}_4$  as a reagent at low pH to assure complete protonation (Goessler and Kuehnelt, 2002). This method is used in this study to prevent interference. Furthermore, as a preliminary step the analytical method was checked for any further interference because Bauxsol could release ions that could interfere with arsenic analyses. A standard curve was prepared by adding 50, 25 and 15  $\mu\text{L}$  of 1 mg/L standard total arsenic solution to 10 mL aliquots of HCl (1.5%) and plotting the standard total arsenic solution added against the absorbance values read from the HGAAS. A second standard curve was prepared in a similar manner, with 1.5% HCl solution prepared using the supernatant remaining after adding 10 g of Bauxsol to 1 L of deionised water, stirring the mixture for 10 min and centrifuging it for 30 min at 4200 rpm. The standard curves obtained using the two solutions are shown in Figure 4, where the similar slopes obtained for both standard curves indicate that Bauxsol does not release interfering ions.

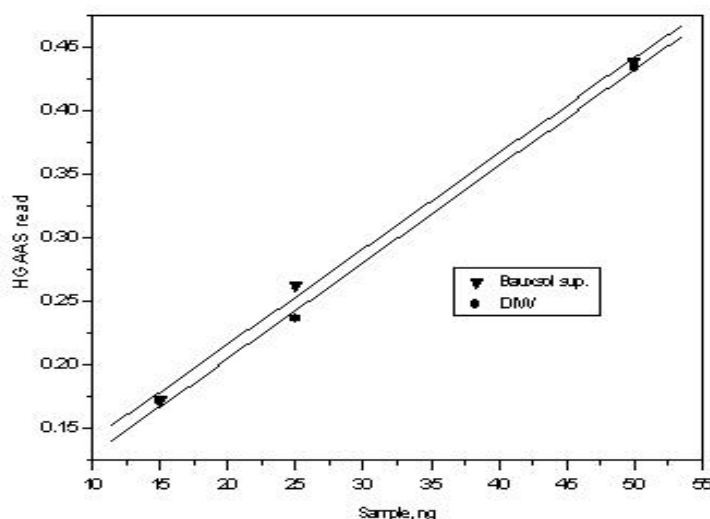
The limit of detection (LOD) for arsenic has been calculated as 2  $\mu\text{g/L}$  with 10 repeated analyses of a sample blank solution and subsequent analysis of the respective calibration curves (Clesceri et al. 1992). It has been found that all calibration curves have high correlation coefficient ( $r^2$ ) values of 0.99 or higher, indicating very good fits.



**Table 6. Instrumental operating parameters for batch and continuous flow hydride generation atomic absorption spectrometry (HGAAS)**

Parameters	Batch flow	Continuous flow	
System type	Hydride generation	Hydride generation	Hydride generation
Element	As	As	As(III)
Matrix	1.5 % HCl	1.5 % HCl	0.1 % HCl
Lamp current, EDL (wt)	8	8	8
Wavelength (nm)	194.3	194.3	194.3
Slit width (nm)	0.7	0.7	0.5
Slit height	Low	Low	Low
Instrument mode	BC <sup>1</sup> on	BC on	BC on
Sampling model	Manual sampling	Manual sampling	Manual sampling
NaBH <sub>4</sub> concentration, % (m/v)	3 in 1% NaOH	3 in 1% NaOH	1 in 0.1% NaOH

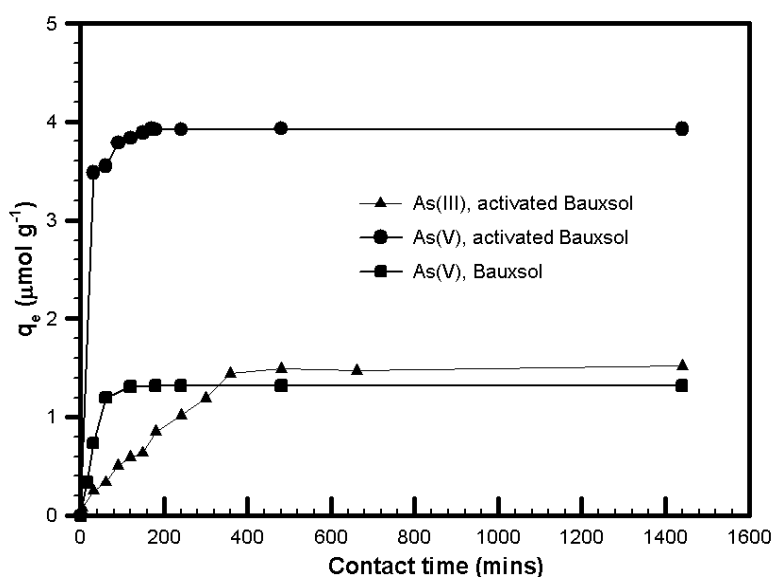
<sup>1</sup> Background correction



**Figure 4. Standard curves of arsenic measurement with hydride generation atomic absorption spectrometry (HGAAS).**

## 5.2. Results of the batch experiments

Batch experiments have been carried out to investigate the sorptive characteristics of the developed sorbents. Herein, the sensitivity of the process for the ionic strength, reaction time, pH, particle size, sorbent dosage, temperature, initial arsenate concentration, and source water composition are tested. Adsorption isotherms are used to determine the sorptive capacities and detailed results can be found in Genç et al. (2003), Genç and Tjell (2003), and Genç-Fuhrman et al. (2004, 2004a, 2004b); a summary is also provided in the later sub-section of this thesis where batch experimental results are discussed.



**Figure 5.** The time dependence of As(V) and As(III) removal using Bauxsol and activated Bauxsol (AB) with reaction conditions: Ionic strength ( $I$ ) = 0.01 M for all; pH = 7.0 for As(V) and As(III) using AB, 7.5 for As(V) using Bauxsol; initial As(V) concentration ( $C_0$ ) = 13.3  $\mu\text{M}$  for Bauxsol and 20.4  $\mu\text{M}$  for AB; initial As(III) concentration ( $C_0$ ) = 14.8  $\mu\text{M}$ ; Bauxsol and AB dosages are = 10 and 5 g/L, respectively.

### 5.2.1. Dependence of the adsorption on ionic strength

Arsenic can be adsorbed to a surface either by the formation of a chemical or a covalent bond (as an inner-sphere type solute complex) or by the power of relatively weak electrostatic bonding forces (as in outer-sphere type solute complex) (Stumm and Morgan, 1996). Studying the influence of ionic strength is a simple approach to distinguish between the inner-sphere and outer-sphere surface complexes when direct evidence from microscopic data is absent. If the adsorption is not affected by the variations of the ionic strength, then an inner-sphere surface complexation should form; whereas if the adsorption is reduced with increasing ionic strength (i.e. due to the competitive adsorption with counteranions), then an outer-sphere surface complexation is more likely (Stumm and Morgan, 1996; Nilsson et al., 1996; Gao and Mucci, 2001). In the present work microscopic studies, e.g. extended X-ray absorption fine structure (EXAFS) are lacking and macroscopic techniques (i.e. investigating the effect of ionic strength) are used. The results show that arsenate adsorption to both Bauxsol and AB is insignificantly affected by the ionic strength and thus, it is postulated that arsenate adsorption onto Bauxsol and AB may take place by the formation of inner-sphere complexation (Genç et al., 2003; Genç-Fuhrman et al., 2004). Note that arsenic adsorption to both iron hydroxide sites (Waychunas et al., 1993; Manning et al., 1998) and aluminum hydroxide sites (Arai et al., 2001) has also been reported to take place mainly via the formation of inner-sphere bidentate surface complexes.

### 5.2.2. Kinetics of the adsorption

In this section, adsorption experiments are carried out to find the equilibrium times for arsenic adsorption onto Bauxsol and AB. It is found that the adsorption of arsenic onto Bauxsol and AB is time dependent, becoming greater with increasing time. The time dependence of arsenate and arsenite adsorption onto AB is given in Fig. 5, where it can be seen that optimal arsenate adsorption onto Bauxsol and AB is attained at the same equilibrium time (i.e. 3 hours), whereas arsenite adsorption onto AB is slower, taking 6 hours (Genç et al., 2003; Genç-Fuhrman et al., 2004, 2004a). The kinetic data also fit well to a first order Lagergren equation. The results of the fitting of the first order Lagergren kinetic equation to the observed data, as in Genç et al. (2003) and Genç-Fuhrman et al. (2004a), show that arsenic adsorption onto Bauxsol and AB takes place at a rate proportional either to the arsenic concentration or to the number of the vacant sorption sites (López et al., 1998). The first-order kinetics also suggests that adsorption is the initial removing mechanism, though it is stressed that kinetic data alone are not sufficient to determine the reaction mechanisms (Sposito, 1986).

### 5.2.3. Effect of pH

The effect of solution pH on arsenic adsorption at various pH values is explored and reported in detail in Genç et al. (2003) and Genç-Fuhrman et al. (2004, 2004a). In all experiments, the pH was measured with the pH electrode calibrated using three buffers (pH 4.0, 7.0, 10.0). Despite the importance of the pH, pH control is not always easily maintained. During the first part of the experiments significant pH changes from the targeted values are observed (Genç et al., 2003), possibly due to the re-equilibration with the surrounding solution of small particles formed during shaking (Gupta and Chen, 1978). Thus the remainder of the adsorption experiments is performed using 0.5 mM NaHCO<sub>3</sub> as a background electrolyte to provide buffering, and to keep the pH within  $\pm 0.1$  pH units.

The results indicate that protonated arsenate is more effectively adsorbed than uncharged arsenite. Arsenate adsorption increases with decreasing pH (for all the tested sorbents) exhibiting the typical sorption behaviour of anions (the adsorption of anions is coupled with the release of OH<sup>-</sup> ions) (Stumm and Morgan, 1996); the H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> form of arsenate is more effectively removed than H<sub>2</sub>AsO<sub>4</sub><sup>2-</sup>. Maximum arsenite adsorption, on the other hand, is recorded at a pH of about 8.5, and declined abruptly at both higher and lower solution pH values under the experimental conditions used (Genç et al., 2003; Genç-Fuhrman et al., 2004a). The observed pH dependence of the arsenate removal is attributed to several factors that are reported in detail in Genç et al. (2003) and Genç-Fuhrman et al. (2004a). In addition to the reported factors another possible reason may be that, at low pH values, metal oxides may form complexes such as Fe<sub>2</sub>(OH)<sub>4</sub><sup>2+</sup>, Fe<sub>3</sub>(OH)<sub>4</sub><sup>5+</sup>, Al<sub>4</sub>(OH)<sub>8</sub><sup>4+</sup> and Al<sub>8</sub>(OH)<sub>20</sub><sup>4+</sup> that can react to form precipitates with the arsenate anion. Analogous results are published elsewhere for the adsorption of arsenic on metal oxides/oxyhydroxides and red mud (Wilkie and Hering, 1996; Meng et al., 2000; Altundoğan et al., 2000, 2002).

#### 5.2.4. Adsorption isotherms

Adsorption data is commonly modelled using the Langmuir isotherm

$$q_e = \frac{(Q_0 b C_e)}{(1 + b C_e)}, \quad [8]$$

its linearized form

$$\frac{C_e}{q_e} = \left( \frac{1}{Q_0 b} \right) + \frac{C_e}{Q_0}, \quad [9]$$

and the Freundlich isotherm

$$\log q_e = \log K + 1/n \log C_e. \quad [10]$$

Here  $C_0$  and  $C_e$  are the initial and equilibrium arsenic concentrations,  $q_e$  is the amount adsorbed at equilibrium,  $Q_0$  is the adsorption maximum, and  $b$ ,  $K$  and  $n$  are isotherm constants. Throughout this work, batch experimental data is found to give good correlation coefficients with both the Langmuir and Freundlich isotherms within the experimental conditions used. In all cases, however, the Langmuir model provided better correlation coefficients. The main underlying assumptions for the application of the Langmuir isotherm are: (i) all surface sites are homogeneous; (ii) the amount adsorbed correlates with the equilibrium solution concentration (Schulthes and Key, 1996); (ii) the adsorption is limited by surface saturation, and is valid for monolayer adsorption on a surface containing a finite number of identical sites; (iii) uniform energies of adsorption on the surface; (iv) no interaction of adsorbate occurs in the plane of the surface (Wilkie and Hering, 1996; Namasivayam et al., 2001); and (v) the adsorption energy is independent of both surface coverage and the formation of monolayer surface coverage (Mohan and Singh, 2002). The Freundlich isotherm, on the other hand, does not predict monolayer coverage, and the surface coverage theoretically increases without limitation with increasing adsorbate concentration (Mohan and Singh, 2002). In this study, the Langmuir isotherm is considered to represent the adsorption data better than the Freundlich model (Genç et al., 2003; Genç-Fuhrman et al., 2004a) despite the heterogeneous Bauxsol surface. Because Bauxsol and AB have limited adsorption capacities, the adsorption can be better defined by the Langmuir isotherm than by the Freundlich isotherm, which assumes exponentially increasing adsorption. Similarly, anion adsorption onto red mud, activated red mud (Altundogan et al., 2000, 2002) and hydrous ferric oxide (HFO) is generally represented with Langmuir type adsorption (Wilkie and Hering, 1996). Note, however, that good linear fits do not always imply the fulfilment of the basic conditions of Langmuir as far as the ion-exchange sorption is concerned (Stumm and Morgan, 1996). Kinniburgh (1986) and Schulthess and Dey (1996) proposed using linear and nonlinear least squares regression analysis for the Langmuir isotherm and state that a good fit to the Langmuir isotherm establishes a platform that allows the process to proceed, but does not confirm that the proposed adsorption mechanism is actually occurring or that monolayer coverage is taking place in the system.

Higher adsorption capacities are obtained from the Langmuir isotherm for AB and ABCS compared to those of Bauxsol and BCS. This may be due to the leaching out of sodalite compounds (Genç-Fuhrman et al., 2004) that may obscure the active sites of the adsorbent (Altundoğan et al., 2002) during the activation; comparison of the XRD scans of Bauxsol and AB confirms the removal of sodalite compounds (Genç-Fuhrman et al., 2004a). The adsorption capacity is significantly lower for arsenite than arsenate for AB, because arsenite is uncharged at the pH values, where the experiments are carried out. The observed arsenite adsorption would be due to the specific adsorption from the action of chemical force attraction leading to surface bonds to a specific site on the AB phase. Observed adsorption capacities for the sorbents used in this study are presented in Table 7 along with the adsorption capacities of some other sorbents reported in the literature for comparison. It is important, however, to note that a direct comparison between the sorbents developed in this study with those presented in the literature is difficult, due to differing experimental conditions and differences in what is reported. It can still be seen from Table 7 that activated carbon, one of the most widely used and well established adsorbents, is not very effective for arsenic removal. This is because most arsenic occurs naturally in anionic forms, and activated carbon is more effective towards organic matter removal (Faust and Aly, 1987). Consequently, it can clearly be seen from Table 7 that the developed sorbents, especially AB and ABCS, have excellent sorption efficiency, as compared to other similar sorbents.

In Table 7 when estimating the cost of a particular sorbent a matrix is prepared using a simple “cost unit system”, which is given in Table 8. Herein several parameters, which are expected to contribute to the total cost, are selected, and each sorbent is evaluated for each parameter using the information (if given) in the cited reference.

Remarks for the adsorption studies: In this study the observed arsenic removal process is probably not a simple adsorption, and the process probably involves more than one arsenic removal mechanism and this may be a particular advantage. However, it is still not fully understood how the removal works and it may not be possible to determine the boundary between simple adsorption, absorption and adsorption precipitation (Apak et al., 1999). Sorption is the common term used for adsorption, surface precipitation or absorption (Sposito, 1986), and it is used here when referring to overall arsenic removal using the developed sorbents. The sorption of arsenic using Bauxsol or AB possibly takes place by three mechanisms: (i) formation of surface precipitates; (ii) co-precipitation (with diffusion or dissolution); and (iii) adsorption (Krauskopf and Bird, 1995). For the sake of simplicity, the initial removal process is assumed to be adsorption and the adsorption data can be studied using the Langmuir and Freundlich isotherms. However, it should be kept in mind that subsequent reactions, such as surface precipitation, solid solution formation and diffusion into the absorbent are also possible in the system.

**Table 7. Comparing several sorbents reported in the literature for arsenic removal at the ambient temperature**

Sorbent	Exp. Set-up	pH <sup>a</sup>		Adsorption maxima, mg/g		C <sub>e</sub> <sup>b</sup> , mg/L		X <sup>c</sup> , g/L	References	Cost parameters <sup>d</sup>										
		As(III)	As(V)	As(III)	As(V)	As(III)	As(V)			a	b	c	d	e	f	g	h	i	j	k
Activated Alumina	Batch	8.3	6.5	0.2	4.1	0.05	0.05	2	Gupta and Chen (1978)											Commercially available
Activated Alumina	Batch	6.9	5.2	15.9	3.5	4.03	7.53	0.1-0.5	Lin and Wu (2001)											Commercially available
Activated Alumina	Batch	-	7.7	-	1.1	-	0.063	0.5-5	Wang et al. (2002)											Commercially available
Activated Bauxite	Batch	7.3	6.4	0.1	2.0	0.05	0.05	2	Gupta and Chen (1978)											No information is given
Activated Carbon	Batch	-	4.0	-	3.5	-	0.01	1	Huang and Fu (1984)											- 2 1 - - 2 1 1 1 1 -
Activated Carbon	Batch	-	3.2	-	0.3	-	0.05	3	Gupta and Chen (1978)											No information is given
Activated Red Mud	Batch	7.25	2-3.5	0.89	0.94	28.65	28.58	20	Altundogan et al. (2002)											- 2 1 2 - 2 - 1 1 1 2
Activated Bauxsol (AB)	Batch	6.8	4.5	0.5	7.7	11.25	0.03	5	Genç-Fuhrman et al. (2004a)											1 - - 1 - 1 - 1 1 - -
Activated Bauxsol (AB)	Batch	-	7.1	-	3.0	-	0.26	5	Genç-Fuhrman et al. (2004a)											1 - - 1 - 1 - - 1 -
ABCS <sup>e</sup>	Batch	-	7.1	-	2.1	-	5	5	Genç-Fuhrman et al. (2004c)											1 - - 1 - 1 - - 1 -
ABCS <sup>e</sup>	Column	-	7.4	-	1.6	-	5	140	Genç-Fuhrman et al. (2004c)											1 - - 1 - 1 - - -
Al-SZP <sup>f</sup>	Batch	-	3-10	-	4.9	-	0.01	5	Xu et al. (1998); Xu et al. (2002)											- 2 - 2 1 1 1 1 - 2
Bauxsol	Batch	-	6.3	-	1.1	-	0.05	10	Genç et al. (2003)											1 - 1 - - 2 - 1 1 1 -
BCS <sup>e</sup>	Batch	-	7.1	-	1.6	-	55	5	Genç-Fuhrman et al. (2004c)											1 - - - - 2 - - 1 -
BCS <sup>e</sup>	Batch	-	4.5	-	3.3	-	4	5	Genç-Fuhrman et al. (2004c)											1 - - - - 2 - 1 1 1 -
BCS <sup>e</sup>	Column	-	5.7	-	6.2	-	1	140	Genç-Fuhrman et al. (2004c)											1 - - - - 2 - 1 1 1 -
Char Carbon	Batch	3.1	3.0	89.2	34.5	536.7	172.3	5	Pattanayak et al. (2000)											- 2 - 2 2 2 - 1 1 - 2
CMFB <sup>g</sup>	Batch	-	3	-	57.9	-	200	1	Loukidou et al. (2003)											- 2 - 2 - 2 - 1 1 - -
Feldspar	Batch	-	4.2	-	0.2	-	-	40	Singh et al. (1996)											1 - 1 - 1 2 - 1 1 1 1
Fe-LDA <sup>h</sup>	Batch	8-10	2-4	43.7	38.5	0.30	0.19	50	Matsunaga et al. (1996)											- 2 - 2 - 2 - 1 1 1 1
Fe <sub>x</sub> (OH) <sub>y</sub> -Montm. <sup>i</sup>	Batch	9	9	13	4	45	55	1.6	Lenoble et al. (2002)											- 2 - 2 - 2 - 1 1 - 2
Ferralite	Batch	-	7.0	-	0.2	-	0.5	5	Bhattacharyya et al. (2003)											1 - 1 - - 2 - 1 1 - 1
Fly ash	Batch	-	4.0	-	27.8	-	-	1	Diamadopoulos et al. (1993)											1 - 1 - 1 2 2 1 1 2
FMO <sup>j</sup>	Batch	6.3	6.5	0.5	15.4	0.016	<0.002	0.4	Chakravarty et al. (2002)											1 - 1 - - 1 3 1 - -
Goethite	Batch	9	9	22	4	30	57	1.6	Lenoble et al. (2002)											- 2 - 2 - 2 - 1 1 - 2
Granular ferric hydroxide	Column	-	7.8	-	8.5	-	0.01	-	Drieaus et al. (1998)											- 2 - 2 1 2 3 1 1 -
Granular ferric hydroxide	Batch	-	7.8	-	8.5	-	0.01	1 <sup>k</sup>	Drieaus et al. (1998)											- 2 - 2 1 2 3 1 1 -
Granular ferric hydroxide	Batch	7.6	7.6	0.1	0.2	0.05	0.05	5	Thirunavukkarasu et al. (2003)											- 2 - 2 - 2 - - - -

Table 7 (Continuing from the previous page)

Sorbent	Exp. Set-up	pH <sup>a</sup>		Adsorption maxima, mg/g		C <sub>e</sub> <sup>b</sup> , mg/L		X <sup>c</sup> , g/L	References	Cost parameters <sup>d</sup>										
		As(III)	As(V)	As(III)	As(V)	As(III)	As(V)			a	b	c	d	e	f	g	h	i	j	k
Hematite ( $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> )	Batch	-	4.2	-	0.2	-	0.11	40	Singh et al. (1996)	1	-	1	-	1	2	-	1	1	1	1
Granular ferric hydroxide	Column	7.6	7.6	0.8	0.9	0.05	0.05	-	Thirunavukkarasu et al. (2003)	-	-	-	-	1	1	-	1	1	2	-
HFO	Batch	-	7.0	-	14 <sup>l</sup>	-	0.07	0.014 <sup>m</sup>	Holm, (2002)	-	-	-	-	-	-	-	-	-	-	-
HFO	Batch	9	9	28	7	20	30	1.6	Lenoble et al. (2002)	-	2	-	2	-	2	-	1	1	-	2
HIX <sup>n</sup>	Column	7.2	7.2	-	-	0.05	0.05	-	DeMarco et al. (2003)	-	2	-	2	2	-	3	-	-	-	-
Iron oxide coated sand	Batch	7.6	7.6	0.04	0.04	0.05	0.05	-	Thirunavukkarasu et al. (2003)	-	2	2	-	-	-	-	-	-	-	-
Iron oxide coated sand	Column	7.6	7.6	0.4	0.3	0.005	0.005	-	Thirunavukkarasu et al. (2003)	-	2	-	-	-	-	-	-	-	-	-
Modified chitosan gel	Column	3	3	80 <sup>o</sup>	230 <sup>o</sup>	450	450	-	Dambies et al. (2002)	-	2	-	2	1	2	-	1	1	-	2
Natural Manganese Oxide	Batch	-	7.0	-	0.2	-	450	10	Ouvrard et al. (2001)	-	2	-	2	1	2	-	1	1	-	2
Red Mud	Batch	9.5	3.2	0.67	0.52	16.7	19.7	20	Altundoğan et al. (2000)	1	-	1	-	1	2	3	1	1	2	2
Synthetic Akaganeite <sup>p</sup>	Batch	-	7.5	-	93.1	-	25	0.5	Deliyanni et al. (2003)	-	2	-	2	1	2	2	-	-	1	2
Synthetic goethite	Batch	-	3-3.3	-	47	-	0.01	1	Matis et al. (1997)	1	-	-	2	-	2	1	0	1	1	-
Ti <sub>x</sub> H <sub>y</sub> -Montm <sup>t</sup>	Batch	9	9	13	2	47	56	1.6	Lenoble et al. (2002)	-	2	-	2	-	2	-	1	1	-	-
Zero-valent iron	Batch	-	7	-	-	-	20-200	2.5	Ramaswami et al. (2001)	-	2	-	2	-	2	-	1	1	-	2
Zero-valent iron <sup>s</sup>	Column	6.5-7.2	-	4.4	-	>0.02	-	74.3	Nikolaïdis et al. (2003)	Commercially available										
Zr-CMA resin <sup>t</sup>	Batch	6.5	4.0	31.7	30.7	<0.01	<0.01	-	Suzuki et al. (2000)	-	2	-	2	2	1	-	1	1	1	-
ZMS <sup>u</sup>	Batch	4.0	4.0	0.02	0.1	0.01	0.01	110 <sup>v</sup>	Elizalde-González et al. 2001	-	2	-	2	1	2	-	1	1	-	-

- Data not available or not relevant; <sup>a</sup> optimum pH value; <sup>c</sup> In the case of column tests the weight of the filter medium is given in g; <sup>d</sup> see Table 8; <sup>e</sup> Tap water is used;

<sup>f</sup> Aluminum-loaded Shirasu-zeolite; <sup>g</sup> Chemically modified fungal biomass (*P. chrysogenum*); <sup>h</sup> Iron(III)-loaded chelating resin with lysine- N<sup>α</sup>, N<sup>α</sup>-diacetic acid; <sup>i</sup> Montmorillonite pillared with titanium(IV); <sup>j</sup> Ferruginous manganese ore; <sup>k</sup> given as gFe/L; <sup>l</sup> mg/gFe; <sup>m</sup> mgFe/L; <sup>n</sup> Hybrid ion exchanger; <sup>o</sup> Given as mg As/g Mo; <sup>p</sup> β-Fe(OH); <sup>r</sup> Montmorillonite pillared with iron(III); <sup>s</sup> Field experiments; <sup>t</sup> Zirconium(IV) loaded polymer resin functionalized with diethylenetriamine-N,N,N',N'-polyacetic acid; <sup>u</sup> clinoptilolite-rich Mexican tuff; <sup>v</sup> given as zeolite in a mass/L.

**Table 8. Cost unit-criteria matrix (used to estimate the cost of the sorbents that are compared in Table 7)**

Cost unit	Criteria
1	a) Adsorbent prepared in laboratory using a cheap method
2	b) Adsorbent prepared in laboratory using an expensive method (or purchased)
1	c) Preparation of the adsorbent requires minimum men power and energy
1+1	d) Preparation of the adsorbent requires skilled men power and significant energy
3	e) Prepared adsorbent is toxic and needs to be handled with care during storage, transportation, and etc.
2	f) The raw material needs to be transported
3	g) Spent adsorbent is toxic and needs to be disposed with special care
1	h) pH needs to be adjusted before the process
1	i) pH needs to be adjusted after the process
1	j) Pre-oxidation of As(III) to As(V) is necessary
2	k) The guideline value of 0.01 mg/L can be not reached, additional treatment is necessary

#### 5.2.4. Modelling arsenate adsorption

In addition to the empirical Langmuir and Freundlich models, surface complexation (SC) modelling is also used to study the molecular description of the arsenate adsorption using AB. Goldberg (1995) reports that the greatest advantage of SC models is that they consider the charge of both the adsorbate ion and the adsorbate surface although the limitation is that they assume homogenous surface functional groups. Constant capacitance models, diffuse layer models, and triple layer models are commonly employed SC models (Manning and Goldberg, 1995; Goldberg and Johnston 2001). Here, diffuse layer modelling (DLM) is used because it is user friendly and no capacitance density (which varies with pH and ionic strength) parameter is required. The FITEQL version 4 (Herbelin and Westall, 1999) and PHREEQC version 2 computer programs (Parkhurst and Appelo, 1999) are used to model the experimental data (Genç-Fuhrman et al., 2004a) but only arsenate modelling is carried out because arsenite adsorption may not be well-defined in the model due to the possibility of heterogeneous oxidation of arsenite (Manning and Goldberg, 1997).

Because SC models assume uniform surface sites, they are commonly applied to well-defined oxides (Meng et al., 2000), and in the present study this requires that the AB surface is represented somewhat simplistically as a single homogenous surface. The DLM modelling is primarily based on the following two assumptions (Goldberg, 1995): (i) all surface complexes are inner-sphere complexes; and (ii) no surface complexes are formed with ions of the background electrolyte. When carrying out the modelling, the intrinsic acidity constants are taken from the literature (Güçlü and Apak, 2000), and best-fit SC constants are calculated with FITEQL model simulations of the experimental data. The FITEQL program uses a nonlinear least squares optimization routine to determine the adsorption constants by minimizing the discrepancies between the calculated and experimental data (Manning and Goldberg, 1997). Good agreement between the experimental and modelling data has been reported in Genç-Fuhrman et al. (2004a). Estimation of the surface complexation constants using FITEQL software and



the use of these constants in the PHREEQC and FITEQL programs demonstrates that the values obtained from FITEQL can be applied in both models to obtain good fits. However, if the reactive surface is assumed to be provided by hydrous ferric oxide only, the fit between model and experimental data is poor and the amount of adsorption is underestimated, indicating that there are more minerals involved in arsenate adsorption on AB than Fe-oxide alone.

#### **5.2.5. Effect of adsorbent dosage**

The dependence of arsenate adsorption on adsorbent dosage with varying amounts of Bauxsol and AB dosages has been examined and details are presented in Genç et al. (2003) and Genç-Fuhrman et al. (2004a). It is found that arsenate removal by both sorbents depends strongly on the sorbent dosage, indicating that adsorption is dependent on the availability of the bonding sites (Pradhan et al., 1999). For example when Bauxsol is used as a sorbent, dosages  $>5$  g/L need to be applied to achieve the WHO standard at circum neutral pH values when the initial arsenate concentration is  $<0.5$  mg/L. Although this is significantly better than the 100 g/L dosage reported previously for red mud (before seawater-neutralisation to form Bauxsol) at pH 3.2 (Altundogan et al., 2000), it is still considered high for practical applications. This limitation can be overcome by enhancing the adsorptive capacity of Bauxsol by the combined acid and heat treatment and producing AB: When AB is used as an adsorbent, 0.4 g/L AB is sufficient to achieve the WHO standards if the initial arsenate concentration is smaller than 0.33 mg/L at nearly neutral pH values.

When the adsorbent dosage of AB is increased from 0.4 to 1 g/L the arsenic binding capacity is increased dramatically. When the dosage is increased further from 1 to 2 g/L, from 2 to 5 g/L and finally from 5 to 10 g/L, the capacity is further increased, but the magnitude of the increase is proportionally less significant with each successive increase. It is postulated that at low adsorbent dosages all types of sites are entirely exposed for adsorption, and the surface may become saturated faster; whereas at higher adsorbent dosages the availability of higher energy sites may decrease (Das et al., 2002).

#### **5.2.6. Effect of source water composition**

Most adsorption studies are carried out using deionised water in single anion systems. However, in real life situations arsenic is always accompanied in water by other ions. Therefore, it is important to explore the effect of source water composition on the process efficiency. With this motivation, considerable attention has been directed towards understanding the effects of  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ , and  $\text{HCO}_3^-$  (common ions in tap water) on arsenate removal using Bauxsol. It is found that all the anions tested, except  $\text{Ca}^{2+}$ , interfere with the arsenic sorption by competing with arsenate for the available surface sites. The suppression of arsenic sorption caused by  $\text{HCO}_3^-$  is much greater than that caused by  $\text{Cl}^-$  (Genç et al., 2003) similar results are reported elsewhere by Matsunaga et al. (1996). The presence of  $\text{Ca}^{2+}$ , however, improves arsenic removal due to favourable electrostatic effects, as it increases the number of positively charged surface sites for the adsorption (Wilkie and Hering, 1996; Genç et al., 2003).

Natural waters are multi-component systems and they can only be described properly if competitive reactions are considered (Nilsson et al., 1996). Thus, additional experiments have been designed to simulate the effects of phosphate ( $\text{PO}_4^{3-}$ ), silicate ( $\text{H}_3\text{SiO}_4^-$ ), sulfate ( $\text{SO}_4^{2-}$ ) and bicarbonate ( $\text{HCO}_3^-$ ) anions on arsenic removal using AB in binary (dual adsorbate) systems. This is motivated by the following two facts: (i) the groundwater in Bangladesh contains high concentrations of phosphate (0.2-3 mg-P/L), silicate (6-28 mg-Si/L) and bicarbonate (50-671 mg/L) (Meng et al., 2001); and (ii) the presence of these anions in source water has been reported to interfere with arsenic removal (Hering et al., 1996; Meng et al., 2000, 2002; Holm, 2002; Wang et al., 2002). A detailed investigation has been carried out to assess the effect of these anions on the arsenate removal using AB at environmentally realistic concentrations to achieve a reasonable estimate of the arsenic removal capacity of AB. Details are presented in Genç and Tjell (2003) and Genç-Fuhrman et al. (2004), and the following results are highlighted. The AB surface is attractive to several anions other than arsenate, and the selectivity of AB on a molar basis is: arsenate > phosphate > silicate > sulfate > bicarbonate > chloride. Moreover, the observed suppression increases with increasing competing anion concentration, and is more pronounced at higher initial arsenate concentrations (Wilkie and Hering, 1996; Genç and Tjell, 2003; Genç-Fuhrman et al., 2004). Phosphate interferes strongly with arsenate adsorption, probably because it shows similar chemical properties and surface complexation behaviour. However, arsenate sorbs more strongly than phosphate possibly because arsenate ions are larger in size and interact greatly with some of the surface  $\text{OH}^-$  groups (O'Reilly et al., 2001). It is noted, however, that although AB has the highest affinity towards arsenate, the other anions are usually present in natural water in much higher concentrations i.e. silicate approximately 1000 times and phosphate 10-100 times greater than arsenic, and they are usually present in combination (Karcher et al., 1999; Holm, 2002).

Competitive adsorption in a multi-component mixture is common, and it is not equivalent to the sum of the respective mono-component adsorptions, primarily due to the complex anion interactions between the absorbable species (Mohan and Singh, 2002). Therefore, the operating capacity of the adsorbent cannot be directly deduced from individual isotherms (Ouvrard et al., 2001; Wu et al., 2002). Although, sulfate and bicarbonate seem to be rather weak suppressors when using AB to remove arsenate; their effect is magnified when they coexist with phosphate and silicate (Genç-Fuhrman et al., 2004b). Thus, despite their minor effects when they are present individually, the combined effects of bicarbonate and sulfate on arsenate removal cannot be ignored. It is suggested that when source water includes the previously mentioned competing anions, using a higher sorbent dosage or lowering the reaction pH may still allow the promulgated standard to be reached (Genç and Tjell, 2003; Genç-Fuhrman et al., 2004b). These findings compare well with previously reported results (Holm, 2002; Meng et al., 2002). In the present study, although all observed suppression can be attributed to anion competition for the available sorption sites, it is also possible that other factors may also influence arsenate adsorption. For example, the presence of the anions may slow reactions and the equilibrium time measured for a single arsenate adsorption system may not be enough to achieve the optimum adsorption in binary or multi-adsorbent systems (Hering and Kraemer, 1994). Thus, the observed inhibition may also be attributed in part to insufficient reaction time.

In addition to the anions tested for interference, some dissolved substances in source water have also been reported to interfere with the mobility of arsenate and arsenite. Of these, natural organic matter (NOM) such as humic and fulvic acids (prevalent constituents of natural waters with concentrations varying between 1 and 50 mg/L) are particularly important. NOM is highly reactive towards both metals and surfaces, and is common in natural waters. The presence of NOM in water can delay the attainment of sorption equilibrium, as well as suppressing the extent of arsenite and arsenate sorption on alumina, goethite and hematite (Xu et al., 1991; Grafe et al., 2001; Redman et al., 2002).

Running additional experiments using real water samples to be treated is recommended to reconcile the observations of arsenate adsorption in laboratory experiments using multi-adsorbent systems and natural water samples. In some instances a cooperative effect is also possible in multi-adsorbent systems; e.g. due to electrostatic effects at oxide surfaces (Wilkie and Hering, 1996). It has also been reported that more sites can be occupied by a mixture of anions than by the individual ions alone (Wu et al., 2002). Furthermore when anions and cations are present together, they may behave quite differently than when they are alone; e.g., in the presence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  the suppression effect of silicate is reduced, possibly due to the neutralisation of negative surface charges (Meng et al., 2000).

#### **5.2.7. Desorption**

Desorption studies have been carried out at various arsenate loadings and pH values to explore the desorption of arsenate from AB under conditions identical to those during adsorption. The results show that a portion of the bound arsenate is not desorbable and indicate that the adsorption is to a large extent irreversible; there is a maximum of 40% desorption at pH 11.6 and even less at lower pH values (Genç-Fuhrman et al., 2004a). Such a low reversibility strongly suggests that physical adsorption alone may not be sufficient to define the system and that chemisorption must be taking place in the system. Note that physical adsorption is an easily reversible non-activated process that involves relatively weak attractive forces (Van der Waals forces) between the adsorbate and adsorbent (Mahuli et al., 1997). The notably low desorption rates found in Genç-Fuhrman et al. (2004a) may also suggest that arsenic that is initially adsorbed by Bauxsol may later be redistributed to become structural components of minerals during recrystallisation (McConchie et al., 1999).

#### **5.2.8. Other considerations**

An appropriate arsenic removal technology must ensure that no harmful chemicals are introduced to the water, and that other aspects of water quality are not adversely affected during arsenate removal (Scott et al., 1995; Ramaswami et al., 2001). To explore this possibility, water samples have been collected at the end of the adsorption studies and analysed for a wide range of contaminants regulated by the WHO for drinking water. The results of these tests show that neither the use of Bauxsol nor the use of AB adds any unwanted ions to the water (Genç et al., 2003; Genç-Fuhrman et al., 2004).

The spent Bauxsol or AB has also been subjected to the Toxicity Characteristic Leaching Procedure (TCLP) to test whether the spent sorbents are toxic. The results show that all tested parameters, including arsenic, are well below the current US EPA TCLP standards (1996). Thus the spent Bauxsol and AB are suitable for disposal in nonhazardous waste landfills including municipal solid waste landfill (Chwirka et al., 2000). Note that compliance with a more stringent TCLP standard may also be possible with the obtained TCLP results for Bauxsol and AB (Genç et al., 2003; Genç-Fuhrman et al., 2004).

## **6. Arsenic removal using Bauxsol or activated Bauxsol in continuous flow system**

This section describes the results of using sorption filters filled with Bauxsol or AB coated sand to remove arsenate from water. Bauxsol coated sand (BCS) and AB coated sand (ABCS) are prepared by mixing Bauxsol or AB with wet sand and drying the coated grains. Further details on the preparation of the granular adsorbents are given in Genç-Fuhrman et al. (2004c). BCS and ABCS are also used in batch experiments to obtain kinetic and isotherm data. High bed volumes are obtained in the column experiments, and it is interesting to note that the adsorption capacities estimated from batch experiments are lower than those estimated from column experiments. This may be partly due to the fact that the adsorption process in a continuous system differs from that in a batch (Gupta et al., 2001). Adsorption of arsenic onto porous BCS or ABCS may take place in three consecutive steps (after Mohan and Singh, 2002): (i) film diffusion, with arsenic transported to the external surface of the adsorbent; (ii) particle diffusion, where some of the arsenic is adsorbed on the surface, and the rest transported within the pores of the adsorbent; and (iii) fast arsenic adsorption on the exterior surface of the adsorbent. Another difference between the column and the batch system is that the equilibrium is not reached in columns due to the continuous arsenate supply to the system (López et al., 1998).

The effects of flow rate, inflow arsenate concentration, and the presence of competing anions has also been evaluated in continuous flow systems. It is found that all tested variables influence the breakthrough curves. For instance, increasing the flow rate or the initial arsenate concentration, as well as adding potentially competing anions to the source water, decreases the number of bed volumes treated before breakthrough. As expected, the inflow arsenate concentration has the greatest effect (Genç-Fuhrman et al., 2004c). When BCS or ABCS columns become exhausted they can be partly regenerated using 0.3 M NaOH solution, and mass balance calculations indicate an overall  $\approx 65$  percent arsenate recovery for BCS and ABCS.

All continuous flow experiments have been carried out using arsenate, assuming that the method would fail to remove arsenite effectively. In natural groundwater, however, the existence of mildly reducing conditions may mean that arsenite is the dominant arsenic species. Hence, it may be necessary to either oxidise arsenite to arsenate before feeding the columns, or to add manganese dioxide (or another suitable oxidant) to the filter medium for an effective and fast oxidation of arsenite to arsenate (Driehaus et al., 1995). It is suggested that, when conducting field experiments using the BCS or ABCS filtration with natural water samples, manganese oxide should be tried in a fixed bed along with BCS and ABCS to oxidise any arsenite present in the groundwater.

## 7. Applicability of the method

In this section the applicability of the use of Bauxsol, acid treated Bauxsol, AB, BCS and ABCS to remove arsenic from drinking water is considered in relation to the likely cost of the sorbents. Red mud is the raw material of the sorbents used in this study and the (qualitative) cost of preparing Bauxsol, acid treated Bauxsol, AB, BCS and ABCS from red mud summarised as follows:

1. Supplying red mud: Red mud can be obtained free from alumina refineries, but transportation of the material may be a concern. Note that alumina refineries are located worldwide, including in areas geographically close to the arsenic contaminated areas (e.g. India). Hence, the transportation cost may not be a serious impediment. For example, the transportation costs of the sorbents from the available areas to the arsenic affected areas might be estimated as US\$16/ton/1000km, as postulated by Bhattacharyya et al. (2003), for the transportation of ferralite in Bangladesh. This figure is used here as an initial approximation.
2. Seawater-neutralisation of red mud: The main costs for this process are of the seawater itself, as well as for the basic labour for mixing and subsequently separating the solid and liquid phases. If the neutralised red mud is to be washed, or dried, or both, these additional requirements may substantially increase costs.
3. pH change: The reaction pH of Bauxsol (fully neutralised) is between 8.2-8.8, which provides the optimum pH for arsenite sorption. Unfortunately, for effective arsenate removal the pH needs to be decreased. Thus, a chemical (e.g. HCl) for reducing the pH and a pH meter to measure the pH should be included in the cost.
4. Acid treatment: Acid treatment may be carried out by boiling HCl and Bauxsol, which requires energy as well as skilled operators to carry out the boiling and the following precipitation processes safely.
5. Heat treatment: Here, a substantial energy input and a suitable kiln or oven is required to carry out the treatment although skilled operators are not required.
6. Coating sand with Bauxsol or AB: Sand and basic labour are needed. After coating BCS and ABCS may be dried either in a kiln or oven or simply under the sun (if possible).

**Table 9. Cost parameters for seawater-neutralised red mud (Bauxsol) and Bauxsol based sorbents**

	Cost parameters					
Sorbents	1	2	3	4	5	6
<b>Bauxsol</b>						
<b>ATB</b>						
<b>AB</b>						
<b>BCS</b>						
<b>ABCS</b>						

Pertinent cost parameters for the preparation of Bauxsol and the other sorbents derived from Bauxsol are given in Table 9; the cost parameter numbers are those presented immediately before the Table 9. The preparation of the sorbents is generally not expensive, although the process may be time consuming and it is unlikely that any of the key steps could be carried out at a local household scale. However, Bauxsol and BCS are easy to prepare and perhaps the best approach would be to prepare the sorbents in a commercial-scale facility and supply them to village-scale operators or households for the preparation and filling of simple flow-through filtration systems. Later more advanced, and possibly cheaper, alternatives may be developed, such as the highly porous Bauxsol pellets recently developed by Virotec international, but this remains a topic for further research (McConchie, 2004).

In relation to the economics of the use of Bauxsol derivatives, it is noted that there is not a great difference in arsenic binding capacity between the acid treated Bauxsol (ATB) and the combined acid and heat treated Bauxsol (AB); i.e. 95 and 100% removal for ATB and AB, respectively. Thus, in the future a more detailed study could be carried out to investigate the sorption characteristics of ATB, and to evaluate whether it is more cost-effective to use simple acid treated Bauxsol compared to AB. Moreover, new blends may be prepared using mixtures of Bauxsol and AB or other similar combinations. There are endless possibilities, depending on the source water composition, pH, initial arsenate concentration, etc.

Although the TCLP test shows that the spent Bauxsol and AB are not toxic, the disposal of spent Bauxsol, AB, BCS and ABCS remains to be addressed. This is an inherent issue with all arsenic removal technologies, because the removed arsenic and the spent sorbent must be placed elsewhere (Ramaswami et al., 2001). The method requires further testing in the field to assess the validity of experimental results obtained in the laboratory for arsenic removal using the developed sorbents. This is necessary, because somewhat lower efficiencies are reported in full-scale treatment plants (Scott, et al., 1995, Johnston and Heijnen, 2001).

Overall, the findings of this study indicate that in an arsenic removal plant where Bauxsol, AB, BCS or ABCS are to be used, arsenic removal may be accomplished by employing the following treatment units: (i) Pre-oxidation (to oxidise arsenite to arsenate); (ii) sorption in a batch or column system (to remove soluble arsenic), and (iii) filtration (to remove particulate arsenic).

## 8. Conclusions and recommendations

The presence of arsenic at concentrations above acceptable standards in drinking water is a significant health concern, because prolonged exposure to elevated arsenic concentrations (even at quite low concentrations) has been linked to several types of cancer. Elevated arsenic concentrations have been detected worldwide in groundwater, with the greatest problems being associated with the high arsenic loads found in large areas of Bangladesh and West Bengal, India. Substantially elevated arsenic concentrations in groundwater are usually the result of arsenic bearing minerals dissolving from weathered rocks and soils under favourable pH and Eh conditions, but in some places elevated arsenic concentrations can result from human activities. In view of the frequency of occurrence of arsenic in groundwaters in many countries, including several of the poorest developing countries, the development of an inexpensive and efficient system for arsenate removal from drinking water is essential, and this study describes a promising approach.

Treatment of water and effluents with solid industrial residues for adsorptive removal of arsenic offers a potentially cost-effective and sustainable approach. In this study seawater-neutralised bauxite refinery residues red mud (Bauxsol) are tested for their ability to remove arsenic from drinking water together with various Bauxsol derivatives (acid treated Bauxsol [ATB], acid and heat treated Bauxsol [AB], Bauxsol coated sand [BCS], and AB coated sand [ABCS]) that were all developed in this study. It is found that all these materials can be effectively used for the removal of arsenic (mainly arsenate) from water down to acceptably low concentrations. Their respective affinities towards arsenic, as well as their optimum operational conditions vary, however. The affinity of the developed sorbents towards arsenic in a decreasing order is  $AB > ATB > ABCS > BCS > \text{Bauxsol}$ , and sorptive capacity of all tested sorbents compares well with the similar unconventional sorbents, and AB, ATB and ABCS can even compete with the pure sorbents such as Fe- and Al- oxides commonly employed for the arsenic removal. This is significant as the cost of the pure sorbents that work well for arsenic removal is a limitation, and the sorbents developed in this study is cost-effective.

The data obtained for the most efficient sorbent AB from batch laboratory tests indicate that the adsorption capacity increases with decreasing pH for anionic arsenate indicating ligand exchange, and somewhat favoured at slightly alkaline pH conditions for uncharged arsenite suggesting specific adsorption or oxidation. It is also found in the batch tests that arsenate adsorption is not sensitive to ionic strength and that the maximum desorption for regeneration is only about 40% at pH 11.6. It is postulated that this notably low desorption may indicate that arsenate removal in the system does not take place by simple adsorption (as a result of electrostatic attraction or ion exchange) alone, but rather by chemisorption which involves inner-sphere surface complexes and strong covalent bonding. Furthermore, the adsorption capacity increases with increasing temperature, with thermodynamic parameters indicating a strong affinity between the adsorbent and the adsorbate that suggests the involvement of chemisorption; this may be particularly advantageous when using the sorbents in warmer climates. Adding more sorbent to the system increases the removal of arsenic but should be held up against practical limitations considerations associated with the use of more sorbent e.g. transportation, safe handling, and storage. Source water composition has a great effect



on arsenic removal efficiency, especially if phosphate and silicate co-exist in the system. Previously it was found that when deionised water is spiked with arsenate at  $<0.33$  mg/L, sorbent dosage as low as 0.4 g/L AB may be enough to achieve the WHO standard of 0.01 mg/L arsenic concentration for drinking water at pH 7.0. In the presence of competing anions such as phosphate, silicate, bicarbonate, and sulfate either the sorbent dosage must be increased, or the pH decreased to a safe level to comply with the standards, or in combination.

Because the fine particle size of Bauxsol and AB can cause problems (e.g. clogging or leakage of the sorbents to the treated water) when used in fixed bed adsorption studies, Bauxsol and AB can be coated onto sand before use in fixed bed adsorption studies. After a simple coating process, Bauxsol coated sand (BCS) and AB coated sand (ABCS) are effectively packed as a filter medium in fixed bed column tests. Experiments carried out to compare adsorption capacities obtained in batch and column systems demonstrate a higher sorptive capacity in the fixed system compared to the batch system although this finding may simply reflect the fact that the equilibrium time used in the batch test was not enough to reach the optimum adsorption. Further studies to elucidate the possibility of re-using regenerated sorbents in terms of their capacity after regeneration is advised along with a cost study addressing the feasibility of regeneration compared to simply dumping the sorbent in a landfill (it is not toxic according to the TCLP results).

The use of the sorbents developed during this study may also produce several other benefits over similar sorbents, because these sorbents will simultaneously remove a wide range of other potentially hazardous trace elements to very low concentrations (McConchie et al., 1999, 2002a) without introducing any other secondary contaminants to the water. These additional benefits could be achieved at no extra cost and because the spent sorbents are not toxic, they can be disposed of without the need for confinement.

When the affinity of commonly used adsorbents towards arsenic is compared with the sorbents developed in this study, it is found that the obtained sorptive capacity is comparable to, or better than, other available sorbents. The use of the developed sorbents to remove arsenic is an effective alternative to more costly pure sorbents; AB and ABCS compare favourably with other sorbents and with conventional precipitation or flocculation methods. Considering the fact that the raw material of the developed sorbents, red mud, is originally an industrial waste material generated in the alumina industry, the developed sorbents should be readily available and inexpensive compared to alternative materials and their use will enhance resource use efficiency.

The developed sorbents still need to be tested using natural water samples before drawing final conclusions and full-scale studies will need to be carried out because laboratory-scale tests may provide only an approximation of processes at pilot- or full-scale levels (Cheng et al., 1994; Scott et al., 1995; Hering et al., 1997); lower efficiencies are often reported in full-scale studies compared to those obtained in the laboratory (McNeill and Edwards, 1995). Furthermore, if the sorbents are to be tested in Bangladesh and India, where traditions and religious beliefs are very important in daily

life, the social acceptance of the sorbent by the local population should also be evaluated because the sorbent is originally a waste material.

The main accomplishments of the study are summarised in the following:

- To the author's knowledge this study is the first to show that the seawater-neutralised red mud (Bauxsol) can be used successfully for arsenic removal from drinking water.
- Several methods are tested to increase the sorptive capacity of Bauxsol, and promising new sorbents are developed and tested for arsenic removal both in batch and continuous flow experiments.
- The developed sorbents especially AB, ABCS and ATB are comparable or better than the commonly used conventional sorbents, such as activated alumina and ferric oxides in terms of arsenic removal efficiency and the associated costs.
- Although several unconventional sorbents have been proposed in the literature for arsenic removal, this study is among the very few to produce information not only on the sorptive capacity of the developed sorbents, but also on the overall sorptive characteristics.

In the light of this investigation, it is concluded that the developed sorbents are ready to be tested in field conditions for arsenic removal using natural groundwater. Point-of-use systems may also be developed using these sorbents.

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